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WATER CHLORINE (RESIDUAL) NUMBER 1

R. J. Lishka, et al

Environmental Control Administration
Cincinnati, Ohio

1969

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Environmental Control Administration

WATER CHLORINE (RESIDUAL) NO. 1

STUDY NUMBER 35

ANALYTICAL REFERENCE SERVICE

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Consumer Protection and Environmental Health Service

WATER CHLORINE (RESIDUAL) NO. 1

STUDY NUMBER 35

Report of a Study Conducted by
ANALYTICAL REFERENCE SERVICE

R. J. Lishka, E. F. McFarren, and J. H. Parker
Division of Criteria and Standards
Bureau of Water Hygiene

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Consumer Protection and Environmental Health Service
Environmental Control Administration
Cincinnati, Ohio 45202
1969

I

FOREWORD

The Analytical Reference Service (ARS) is conducted by the Bureau of Water Hygiene of the Environmental Control Administration to evaluate laboratory methods in the environmental field. Cooperative studies by member organizations, who analyze identical samples and critically review methodology, provide the mechanism for:

> Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.
>
> Exchange of information regarding method characteristics.
>
> Improvement or replacement of existing methods by development of more accurate procedures, and development of new methodology for determination of new pollution compounds.

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the membership, consultants, and the ARS staff. Notice of each study is sent to the entire membership. To those who desire to participate, a portion of the study sample is sent, along with data forms for reporting numerical values, a critique of the procedures used, comments on modifications, sources of error, difficulties encountered, or other pertinent factors. The results and comments received are compiled, and a report of each study is prepared.

Now primarily directed toward examination of water, in the past studies have included methods for analysis of air, milk, and food. Some studies are periodically repeated for the advantage of new members, the evaluation of new methods, or the reevaluation of existing methods.

The selection of studies is guided by requests from standard methods committees and the responses to questionnaires periodically circulated among the membership, which now includes 294 Federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

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STUDIES COMPLETED AND REPORTED

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium. Studies completed in 1956, 1958, and 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc. Studies completed in 1957 and 1962. These same metals plus silver. Study completed in 1965. Except for the substitution of magnesium for aluminum, these same metals were analyzed by atomic absorption in 1967. Copper, manganese, and aluminum in the presence and absence of interferences. Study completed in 1969.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation by a specified procedure. Studies completed in 1958 and 1961. Fluoride by ion-exchange and fluoride electrode. Study completed in 1969.
Water-Radioactivity	Gross beta activity. Studies completed in 1959 and 1961. Gross beta and strontium-90 activity. Study completed in 1963.
Water-Surfactant	Surfactant in various waters. Studies completed in 1959, 1963, and 1968.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand. Study completed in 1960. Chemical oxygen demand. Study completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium. Study completed in 1962. These same metals plus vanadium. Study completed in 1966.
Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification. Study completed in 1964.
Water-Nutrients	Silicate, phosphate, ammonia nitrogen, organic nitrogen, and nitrate nitrogen. Study completed in 1966.

Water-Phenols	Phenol and 2, 4-dichlorophenol in water by two specified methods. Study completed in 1966.
Water-Cyanides	Potassium cyanide and potassium ferricyanide in water by two specified methods. Study completed in 1967.
Water-Chlorine	Free and combined chlorine by nine different methods. Study completed in 1969.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass-fiber, high-volume filter mats. Study completed in 1958.
Air-Lead	Filter paper tape impregnated with lead. Study completed in 1961.
Air-Particulates	Microscopic identification of some common atmospheric particulates. Study completed in 1964.
Air-Sulfur Dioxide	Sulfur dioxide in air by a specified method. Study completed in 1963.
Water-Pesticides	Lindane, heptachlor epoxide, DDE, and dieldrin in water. Study completed in 1965. Lindane, heptachlor, aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, endrin, o,p'-DDT, p,p'-DDT, and methoxychlor in water. Study completed in 1968.
Food-Pesticides	DDT in milk. Study completed in 1962. Lindane, heptachlor epoxide, DDE, and dieldrin in milk. Study completed in 1965.

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PREFACE

The chlorination of water supplies accomplishes, in addition to the destruction of microorganisms, a number of other objectives. These include the improvement of the water as a result of the reaction of the chlorine with ammonia, iron, manganese, sulfide, and proteineaceous substances. On the other hand, the reaction of chlorine with compounds such as phenol may also result in the production of undesirable taste and odor compounds. If the chlorination is carefully controlled, however, even the latter can be improved.

In any case, as a result of chlorination, one of the most commonly performed chemical determinations is the measurement of free available or combined available chlorine in water. At present, there are five methods in the 12th edition of Standard Methods for the Examination of Water and Wastewater for the determination of free and combined chlorine. These are the following: iodometric (method A), orthotolidine (methods B and C), orthotolidine-arsenite (method D), amperometric titration (methods F and G), and ferrous titrimetric (method H). Method E (drop dilution method) was not included in this study, since it is designed only for large (greater than 10 mg/liter) chlorine concentrations.

In addition, four new analytical methods have been proposed for inclusion in the 13th edition. These are the following: methyl orange, leuco crystal violet, ferrous-DPD, and stabilized neutral orthotolidine (SNORT).

Unfortunately, none of these have been studied collaboratively, primarily because no one has been able to determine how to prepare a chlorine solution that would remain stable for several months. It has, however, been possible to concoct some stable dry standards. In the latter case, there is perhaps another problem in that there may be some question about whether each measured dry aliquot is exactly equivalent to every other aliquot since these standards are mixtures of at least two chemicals. In any case, because of the large number of methods available and the lack of any data on their usefulness, this study was undertaken in an effort to evaluate and perhaps eliminate some of them.

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ACKNOWLEDGMENTS

Michael J. Taras, Chairman, Joint Editorial Board of Standard Methods for the Examination of Water and Wastewater suggested this study to evaluate and compare four proposed chlorine methods and five methods currently in Standard Methods. He also provided copies of the proposed methods. (See Appendices A, B, C, and D.)

Robert T. Williams, Chief, Analytical Applications Laboratory, Waste Identification and Analysis Activities, Cincinnati Water Research Laboratory, Ohio River Basin Region, provided referee results for the samples used in this study.

Lawrence J. Kamphake, of the same laboratory, suggested the use of halazone as a stable, dry sample containing both free and combined residual chlorine.

Dr. J. Donald Johnson, Department of Environmental Sciences and Engineering, University of North Carolina, suggested the use of a mixture of HTH and sodium chloride to prepare a stable, dry sample containing free chlorine and the addition of ammonia chloride solution to provide another sample containing combined chlorine. He also reviewed the final draft of this report and served as a referee by analyzing both pilot and master samples by several methods.

Dr. George P. Whittle, Department of Civil Engineering, University of Alabama, the author of the leuco crystal violet method, reviewed the final draft of this report.

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PARTICIPANTS IN THIS STUDY

Atomic Energy Authority, Didcot, Berkshire, England
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Calgon Corporation, Pittsburgh, Pennsylvania
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California Water Service Company, San Jose
Chicago Bureau of Water, Illinois
City of Dallas, East Side Purification Plant, Mesquite, Texas
City of Flint Water Plant, Michigan
Connecticut State Department of Health, Hartford
Dalecarlia Filter Plant, Washington, D.C.
Denver Board of Water Commissioners, Colorado
Department of Health and Hospitals, St. Louis, Missouri
DHEW, PHS, Northeast Marine Health Sciences Laboratory, Narragansett, Rhode Island
Department of Municipal Laboratories, Hamilton, Ontario, Canada
Department of Public Health, Edmonton, Alberta, Canada
Fresno Department of Public Health, California
Hach Chemical Company, Ames, Iowa
Hammond-Montel, Inc., Elmhurst, New York
Holzmacher, McLendon and Murrell, Melville, New York
Hydro Research Laboratories, Pontiac, Michigan
Idaho Department of Health, Boise
Illinois State Water Survey, Peoria
Illinois State Water Survey, Urbana
Infilco Products, Fuller Company, Tucson, Arizona
Institute of Environmental Sanitation, Taipei, China
Isotopes - A Teledyne Company, Sandusky, Ohio
Los Angeles County Flood Control District, California
Los Angeles Department of Water and Power, California
Mahoning Valley Sanitary District, Youngstown, Ohio
Maryland State Department of Health, Baltimore
Massachusetts Department of Health, Amherst
Mekoroth Water Company, Bnei-Brak, Israel
Memphis Light, Gas and Water Division, Tennessee
Metropolitan Corporation of Greater Winnipeg, Manitoba, Canada
Metropolitan Sanitary District of Greater Chicago, Cicero, Illinois
Metropolitan Utilities District, Omaha, Nebraska
Ministere de la Sante du Quebec, Montreal, Canada
Minnesota Department of Health, Minneapolis
Minneapolis Water Department, Minnesota
New Jersey State Department of Health, Trenton
New York State Conservation Department, Scottsville
New York State Department of Health, Albany
Newcastle and Gateshead Water Company, Newcastle Upon Tyne, England
North Carolina State Department of Water and Air Resources, Raleigh

North Jersey District Water Supply Commission, Wanaque, New Jersey
Ohio Department of Health, Columbus
Orange County Air Pollution Control District, Anaheim, California
Oregon State Board of Health, Portland
Osaka City Institute of Hygiene, Japan
Pacific Engineering Laboratory, San Francisco, California
Pan American World Airways, Patrick AFB, Florida
Pennsylvania Department of Health, Harrisburg
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Philadelphia Water Department, Torresdale Laboratory, Pennsylvania
Regional Environmental Health Laboratory (LSGHM), McClellan AFB, California
Regional Environmental Health Laboratory (SGHK), Kelly AFB, Texas
Research Institute for Public Health, Delft, Netherlands
St. Louis County Water Company, University City, Missouri
Sandia Corporation, Albuquerque, New Mexico
Santa Clara County Health Department, San Jose, California
Scientific Research Council, Kingston, Jamaica, West Indies
South Carolina State Board of Health, Columbia
Springwells Filtration Plant, Dearborn, Michigan
U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, Maryland
USDI, FWPCA Ohio River Basin Project, Evansville, Indiana
USDI, FWPCA, Raritan Arsenal Depot, Edison, New Jersey
USDI, Geological Survey, Little Rock, Arkansas
University of Alabama, University City
Vermont State Public Health Laboratory, Burlington
Washington State Department of Health, Seattle
Washington State University, Pullman
Yonkers Water Bureau, New York

ABSTRACT

In this study each participant was shipped three vials of dry powder and a sealed glass ampoule of solution which, when dissolved and mixed according to instructions, provided samples containing both free and combined chlorine. Each analyst was requested to use three preselected methods from the nine being studied. A total of 72 participants submitted results indicating that the best accuracy and precision was obtained by use of the ferrous-DPD method, followed closely by the methyl orange, SNORT, and amperometric methods. The leuco crystal violet procedure also gave good results in the analysis of two of the samples but poor on a third containing a hydrolyzable chlorine (dichloroamide), which may simply indicate that the method is more specific for free chlorine than any of the others are. The poorest results were obtained by the use of the other three orthotolidine procedures. It is likely that the greatest potential source of error was in the use of distilled water that was not completely free of chlorine or free of chlorine demand.

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WATER CHLORINE (RESIDUAL) NO. 1

DESIGN OF THE STUDY

In order to obtain maximum stability, the samples were prepared as dry powders and shipped in small screwcap vials containing about 1 gram of each of the following mixtures:

Sample 1 consisted of finely ground halazone tablets made by Abbott Laboratories. The manufacturer states that the tablets contain 2.97 percent active ingredient which is p-(dichlorosulfamyl) benzoic acid and 97.03 percent inert ingredient consisting of sodium borate and chloride. The exact amounts of the latter are not specified.

Sample 2 was prepared by thoroughly mixing 19.2 grams of Olin Matheson granular HTH (70% available chlorine) with 120 grams of C. P. sodium chloride. Before mixing, both the HTH and sodium chloride were ground with a mortar and pestle, and only those portions that passed through a 60-mesh sieve were used.

Sample 3 was prepared by thoroughly mixing 14.4 grams of Olin Matheson granular HTH with 120 grams of C. P. sodium chloride. As with sample 2, both were ground with a mortar and pestle and passed through a 60-mesh sieve before mixing. Also sent with this sample was a glass ampoule containing approximately 20 ml of an ammonia chloride-borate buffer solution. This solution was prepared by dissolving 15 grams of ammonia chloride and 5.7 grams of sodium tetra-borate in 3 liters of distilled water.

On receipt of these samples, the participants were instructed to prepare them for analysis as follows:

Sample 1 - Weigh out approximately 0.1 g and make up to a volume exactly equivalent to 10,000 times the sample weight in g. For example, if 0.0948 g was weighed out, dissolve in 948 ml of chlorine-free, chlorine-demand-free water, measured in a graduated cylinder. The sample is now ready for analysis. Do not dilute any further.

Sample 2 - Weigh out approximately 0.1 g as was done for sample 1 and dilute to volume in the same manner. Dilute 100 ml of this solution to 1 liter using chlorine-free, chlorine-demand-free water, before undertaking analysis.

Sample 3 - Weigh out approximately 0.1 g as was done for sample 1 and 2 and dilute to volume in a like manner. To a 1 liter volumetric flask, add 2 ml of the provided ammonium chloride-borate buffer solution, 100 ml of chlorine-free, chlorine-demand-free water, and then exactly 100 ml of the above-prepared sample 3 solution. (Caution:

always add the chlorine solution to the ammonia solution and not vice versa.) Finally, dilute to 1 liter with chlorine-free, chlorine-demand-free water.

Instructions for the preparation of chlorine-demand-free water were sent with the samples and read as follows: Add sufficient chlorine to distilled water to destroy the ammonia. The amount of chlorine required will be about 10 times the amount of ammonia nitrogen present; in no case should the initial residue be less than 1.0 mg/liter free chlorine, but generally this amount will be sufficient. Allow the chlorinated distilled water to stand overnight or longer, then expose to direct sunlight until all residual chlorine is discharged (usually about 1 day). Since water used for preparation and dilution of samples must also be free of chlorine, this water should be checked for absence of chlorine before use.

The concentrations of free and combined chlorine in these samples were such that when the participants prepared the samples as instructed, they would approximate chlorinated water supplies. Since the materials commercially available and of necessity used in the preparation of these samples do not permit the calculation of an accurate theoretical chlorine content, the mean of the results obtained by two referee laboratories on analysis by amperometric titration[8] have been used (see Table 1). These values agree very closely with the results submitted by another referee laboratory using these three other methods: SNORT,[4] ferrous-DPD,[3] and iodometric.[5]

Table 1. COMPOSITION OF SAMPLES

	mg/liter in diluted sample		
	Sample 1	Sample 2	Sample 3
Free chlorine	0.83	0.80	0.04
Total chlorine	1.83	0.84	0.64
Combined chlorine	1.00	0.04	0.60

Theoretically, however, sample 2 contained only free chlorine, and sample 3 only combined chlorine. Thus, the small values indicated for combined chlorine in sample 2, and for free chlorine in sample 3 are artifacts due to the inability of the method to determine lesser amounts.

In the announcement of this study, participants were provided with

copies of four new methods for the analysis of chlorine that have been proposed for inclusion in the 13th edition of Standard Methods for the Examination of Water and Wastewater, and were requested to choose at least three methods from these and the five other methods for chlorine in the present edition of Standard Methods. They were further told that in order to accomplish the objective of obtaining an approximately equal number of data on each method, they would be requested to analyze the samples by the three methods of their choice only if their choices were rather equally distributed. As it turned out, their choices were rather equally distributed, and it was necessary to request only a few laboratories to analyze the samples by a method other than the three they had indicated as their choice. This was necessary in order to obtain some overlap of laboratories submitting results on the different methods.

The participants were further instructed to analyze the samples only for free and total chlorine. Hence, where combined chlorine is reported in this report, it is obtained by difference.

TREATMENT OF THE DATA

After the results of analysis were received, the data were coded and analyzed by computer for normality of distribution and subsequent rejection of outliers (see Appendix G) that were nonrepresentative because of errors in calculation, dilution, or other indeterminate factors.

The results for each method were also plotted on normal probability paper as a visual check on normality of distribution and the possible presence of outliers. A rather large number of apparent outliers that were not rejected by the statistical tests programmed into the computer were investigated more closely. It was found that certain grossly erroneous results submitted by specific laboratories exhibited a pronounced bias that was similar in each method used by the particular laboratory. Since it was obvious that a common factor such as incorrectly prepared samples, bad dilution water, or incorrectly standardized chlorine reference solutions was responsible, these values also were rejected. A special case was the large number of outliers obtained for the free and combined chlorine measurement in sample 1 by amperometric titration, where it was evident that a high free-chlorine result and a low combined-chlorine result were due to titration for free chlorine at a low pH, probably caused by failure to rinse the titration cell properly after titration for total chlorine. After rejection of outliers, the data were then statistically analyzed by computer for precision and accuracy (see Appendix F), and finally, their precisions and accuracies were compared for significance of differences (see Appendix H).

Bar graphs are included in the text to provide a pictorial display of the data. Rejected values are indicated by broken bars or labelled outliers, and values are given for bars off the scale of the chart.

RESULTS

Sample 1: 0.83 mg/liter free, 1.00 mg/liter combined, and 1.83 mg/liter total chlorine (Table 1; Figures 1 through 12)

This sample was designed to provide both free and combined chlorine by the use of halazone as the active ingredient.

In the determination of free chlorine in sample 1, the mean value obtained by the SNORT[4] method was not significantly different from the referee value, and nearly as good accuracy was obtained by the ferrous-DPD[3] and methyl orange[1] methods. The precision of the ferrous-DPD and SNORT methods was significantly better than that of any of the others, and the amperometric[8] method was not far behind.

In the measurement of total chlorine, the mean values obtained by the ferrous-DPD and methyl orange methods were not significantly different from the referee values. The amperometric method produced nearly as good results. On the other hand, the orthotolidine[6] and orthotolidine-arsenite[7] methods were by far the worst. The precision of the ferrous-DPD and the amperometric methods was significantly better than that of all the others.

In the determination of combined chlorine, the mean values obtained by the use of the methyl orange and the ferrous-DPD methods were not significantly different from the referee value, and the precision of the ferrous-DPD method was significantly better than that of all the others.

In the measurement of free, combined, and total chlorine in sample 1 by the leuco crystal violet[2] method, a very interesting phenomenon occurred.

It appeared that the leuco crystal violet results fell into two groups (see Figures 1, 2, and 3). The one group measured very little free chlorine but obtained high combined-chlorine results, which agrees with ARS findings. The other group reported much higher free-chlorine results but still were below the referee value, and their combined-chlorine results were also low. Obviously, the results obtained by this group were due to some differences in technique or in the interpretation of the application of the procedure. It is also of interest to note that the first group, which obtained the lowest free-chlorine values and presumably did the procedure correctly, also obtained the best total-chlorine results (see Figure 3).

Table 2. SUMMARY OF DATA ON SAMPLE 1
(0.83 mg/liter free, 1.00 mg/liter combined, and 1.83 mg/liter total chlorine)

Method	Determination	Number of results	Number of outliers	Mean	Mean error	Standard deviation	Relative error	Relative std. dev.	95% tol. limits
Methyl orange	Free	26	2	0.647	-0.183	0.341	22.0	52.7	0.890
	Combined	23	4	1.007	+0.007	0.163	0.7	16.2	0.436
	Total	26	1	1.698	-0.132	0.338	7.2	19.9	0.884
Leuco crystal violet	Free	18	0	0.331	-0.499	0.372	60.1	112.2	1.048
	Combined	18	0	1.159	+0.159	0.572	15.9	49.3	1.612
	Total	18	0	1.491	-0.339	0.483	18.6	32.4	1.362
Ferrous-DPD	Free	17	3	0.710	-0.120	0.145	14.5	20.4	0.414
	Combined	17	3	1.063	+0.063	0.077	6.3	7.2	0.221
	Total	19	1	1.751	-0.079	0.164	4.3	9.4	0.457
SNORT	Free	15	2	0.899	+0.069	0.207	8.3	23.0	0.613
	Combined	14	2	0.861	-0.139	0.186	13.9	21.6	-----
	Total	17	1	1.603	-0.227	0.419	12.4	26.1	1.198
Iodometric	Total	32	0	1.524	-0.306	0.360	16.7	23.6	0.909
Orthotolidine	Free	17	0	0.525	-0.305	0.341	36.8	65.0	0.975
	Combined	15	2	0.420	-0.580	0.160	58.0	38.2	0.474
	Total	18	0	1.073	-0.757	0.343	41.4	31.9	0.966
Orthotolidine-arsenite	Free	23	0	0.500	-0.330	0.323	39.8	64.6	0.862
	Combined	22	1	0.376	-0.625	0.168	62.4	44.8	0.454
	Total	23	0	0.923	-0.907	0.323	49.6	35.0	0.863
Amperometric	Free	19	6	0.581	-0.249	0.237	30.0	40.8	0.660
	Combined	19	6	1.112	+0.112	0.161	11.2	14.5	0.449
	Total	24	1	1.669	-0.161	0.209	8.8	12.5	0.553
Ferrous-OT	Free	18	2	0.516	-0.314	0.282	37.8	54.6	0.794
	Combined	18	2	0.824	-0.176	0.258	17.6	31.3	0.726
	Total	19	1	1.359	-0.471	0.357	25.7	26.3	-----

----- Tolerance limits were not calculated since the data is non-normal.

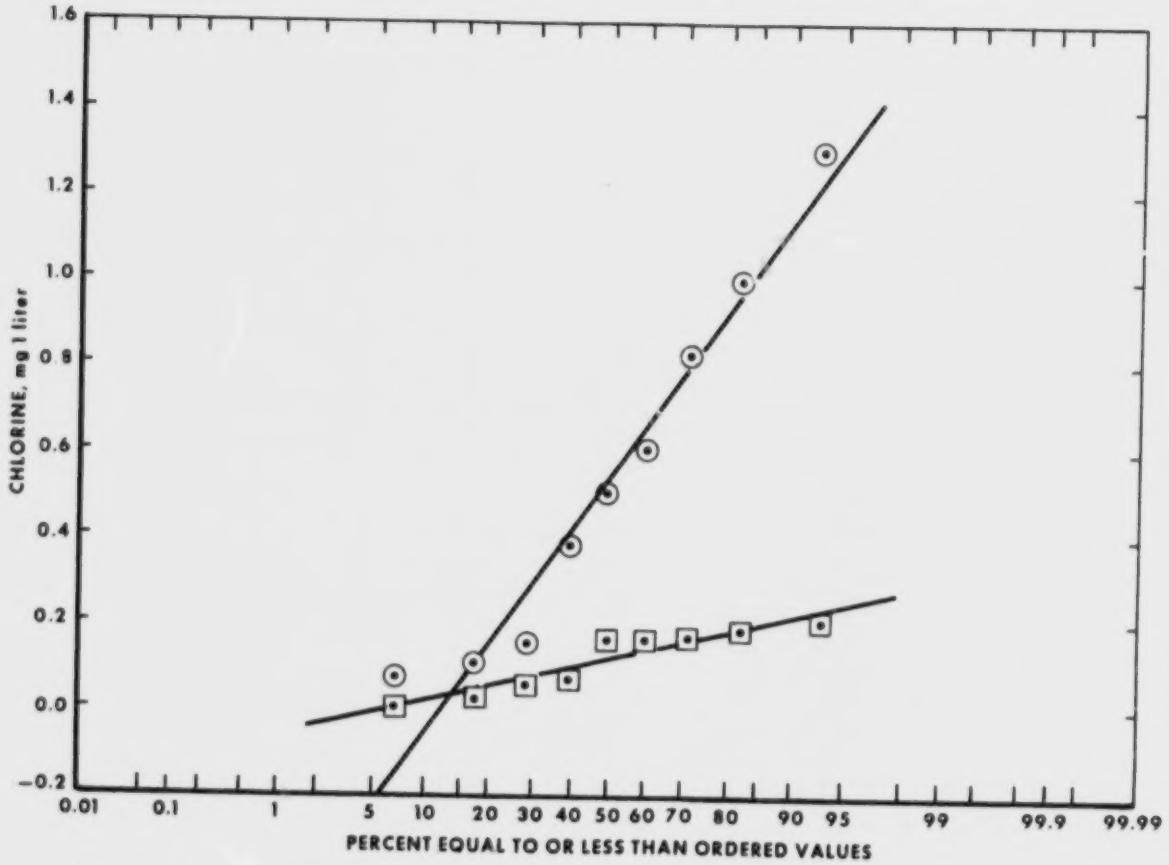

Figure 1. Probability plot for free chlorine in sample 1 by leuco crystal violet method.

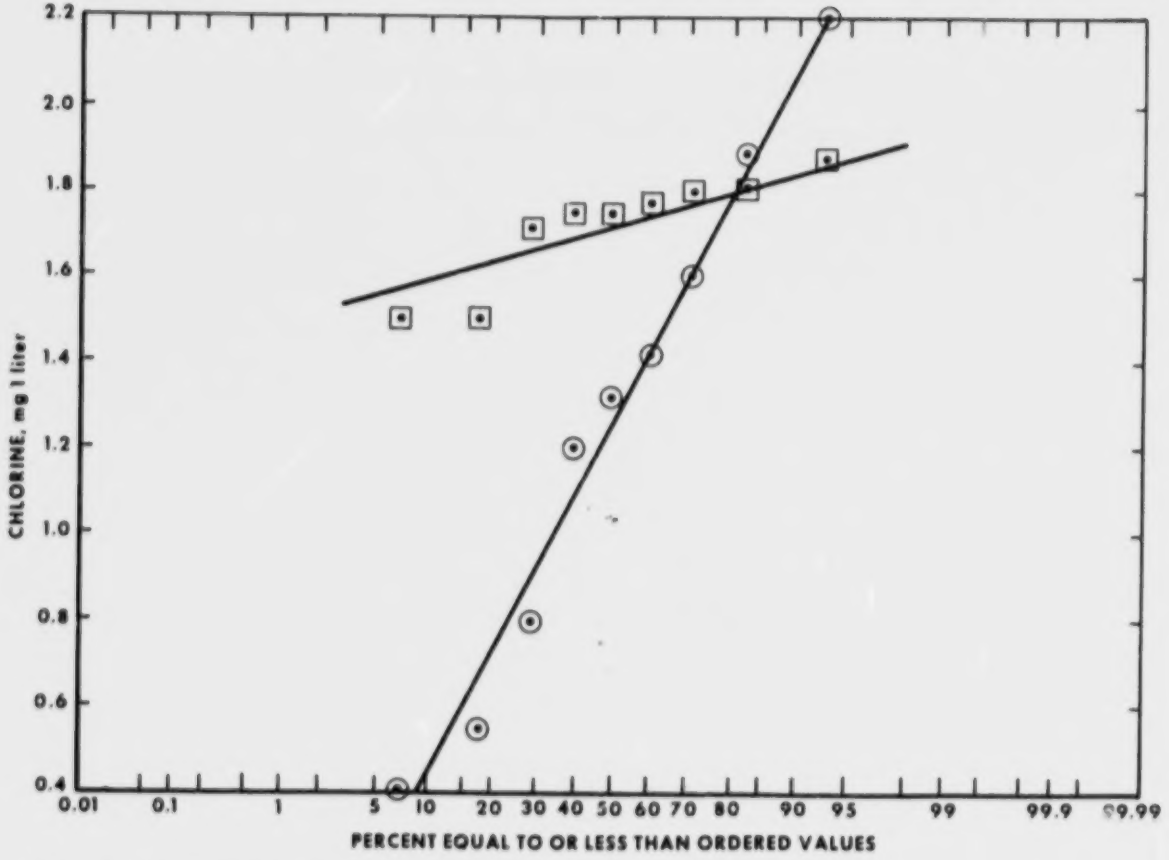

Figure 2. Probability plot for combined chlorine in sample 1 by leuco crystal violet method.

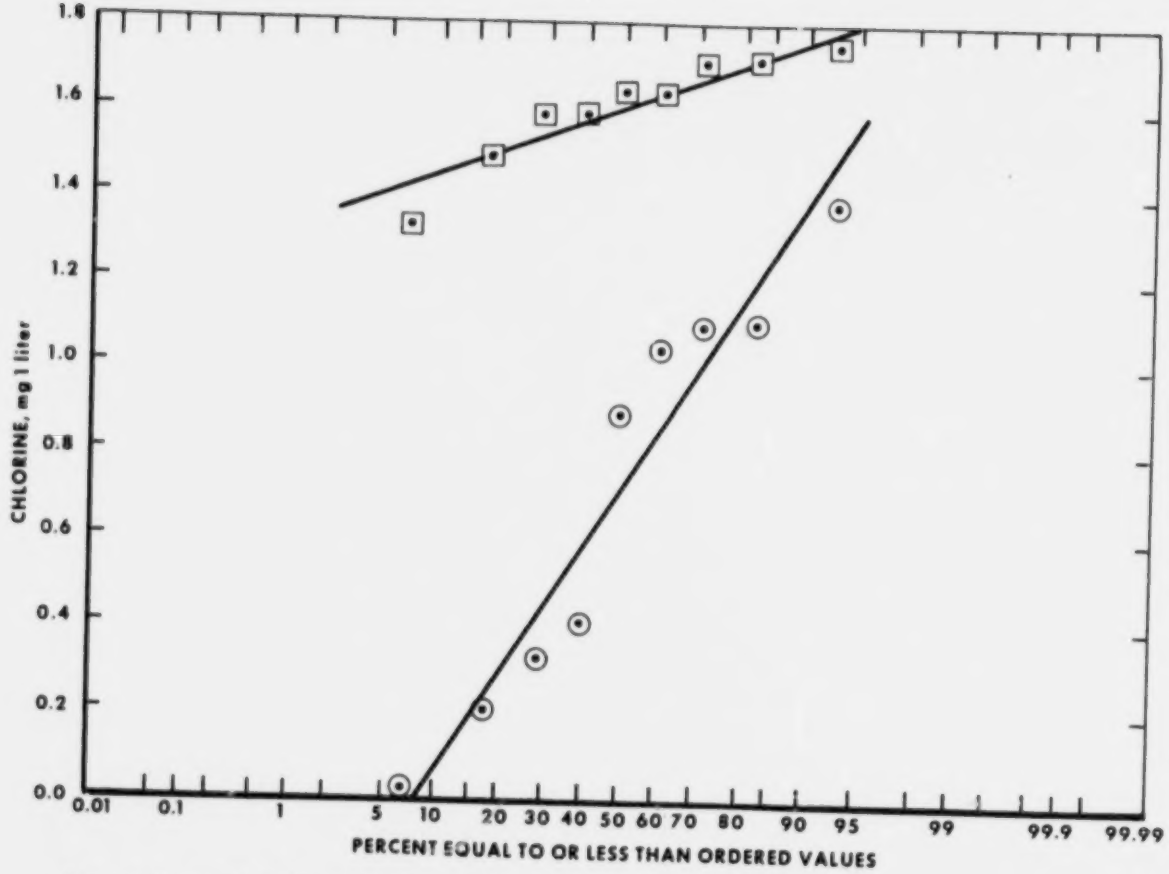

Figure 3. Probability plot for total chlorine in sample 1 by leuco crystal violet method.

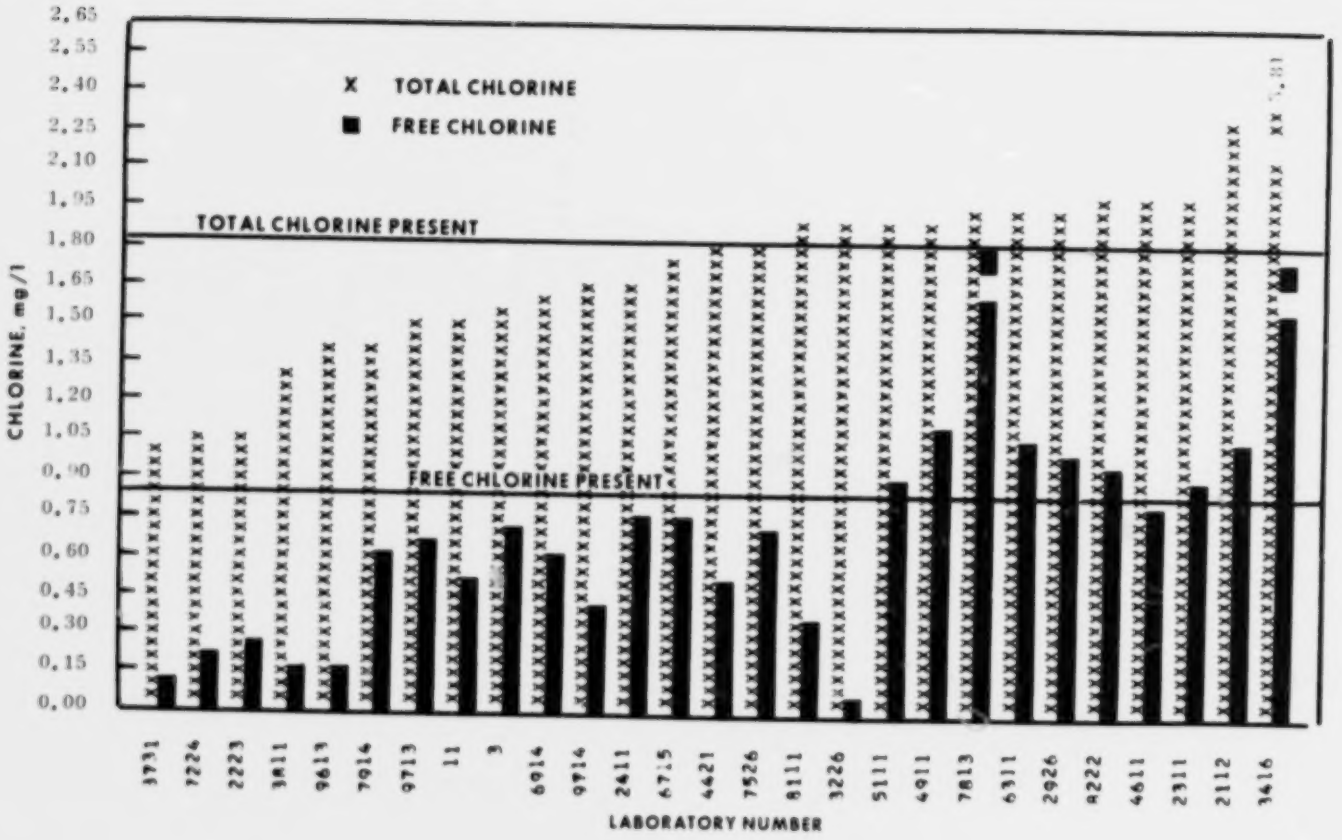

Figure 4. Bar graph for residual chlorine in sample 1 by methyl orange method.

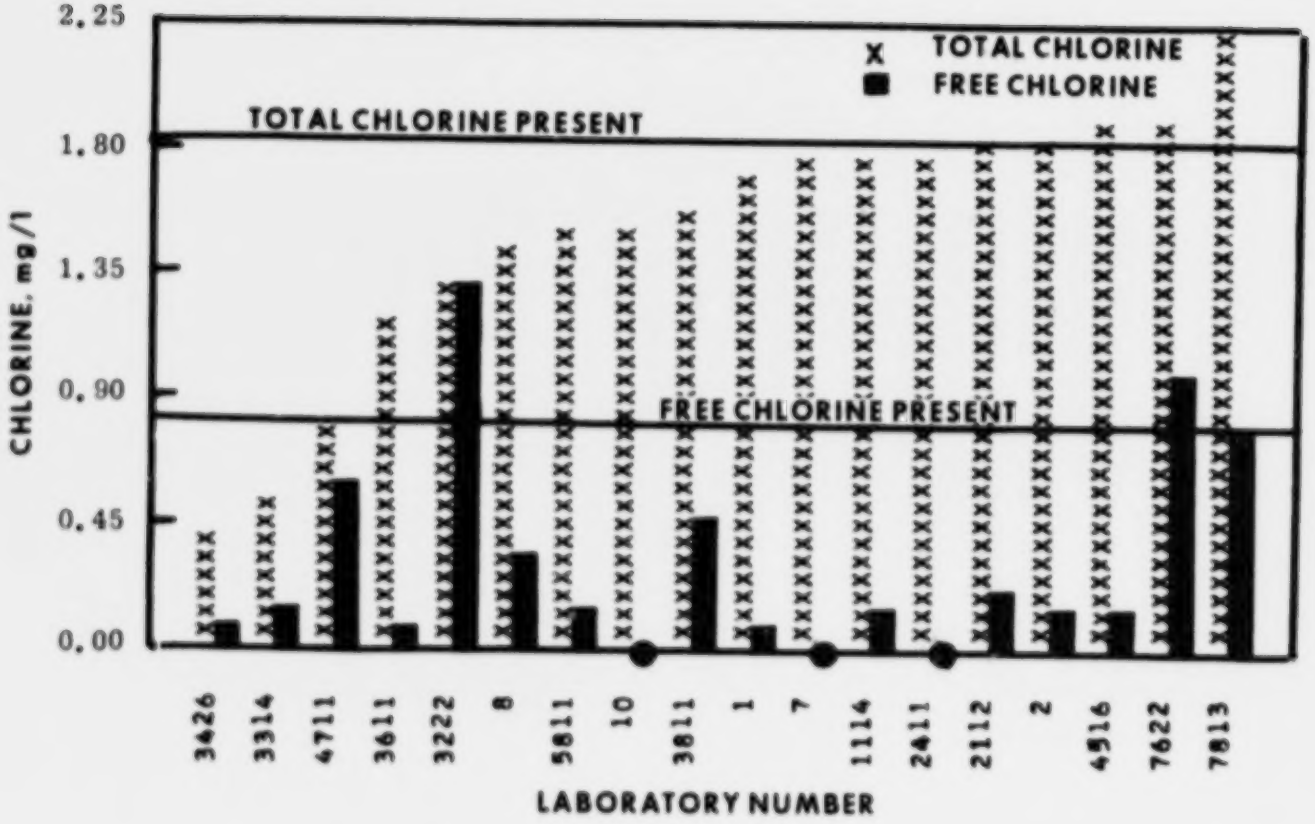

Figure 5. Bar graph for residual chlorine in sample 1 by leuco crystal violet method.

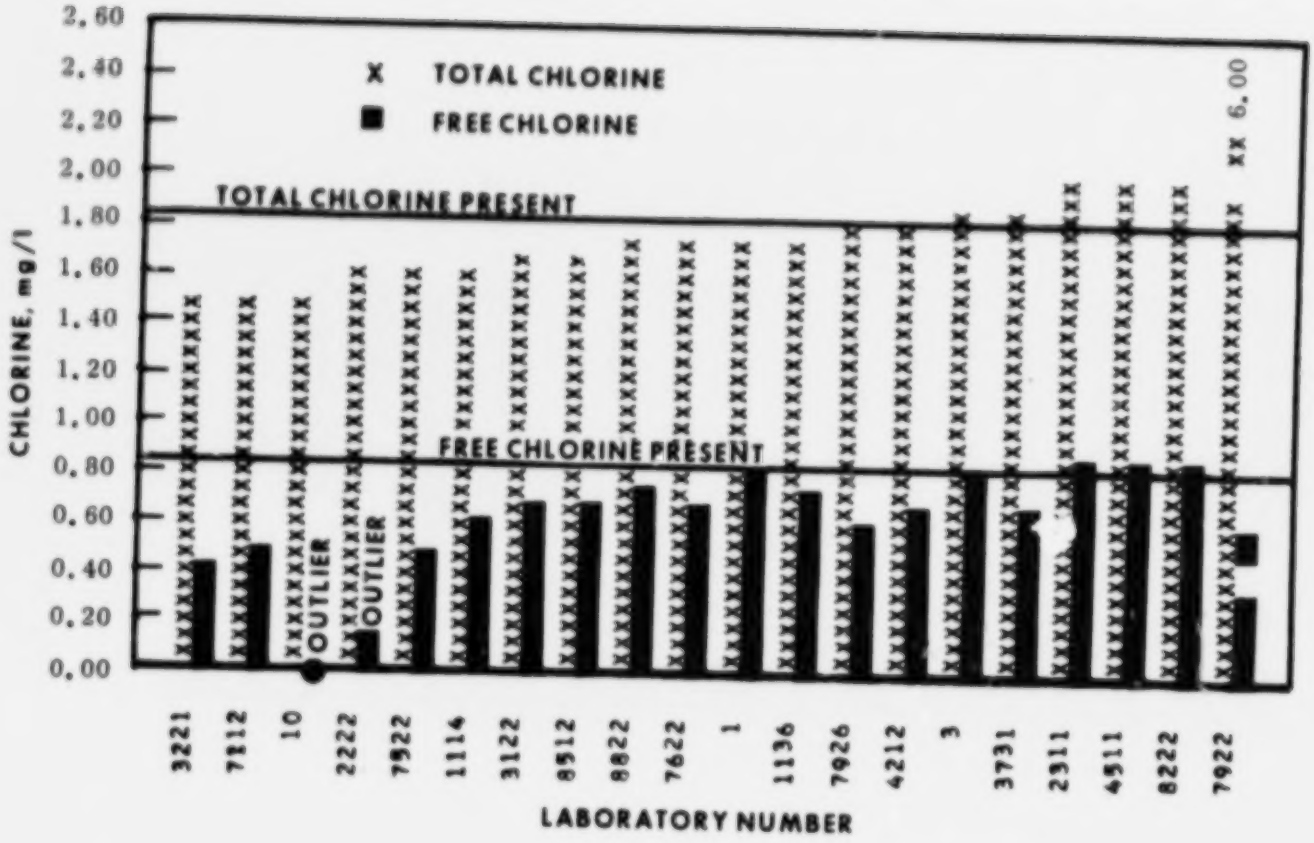

Figure 6. Bar graph for residual chlorine in sample 1 by ferrous-DPD method.

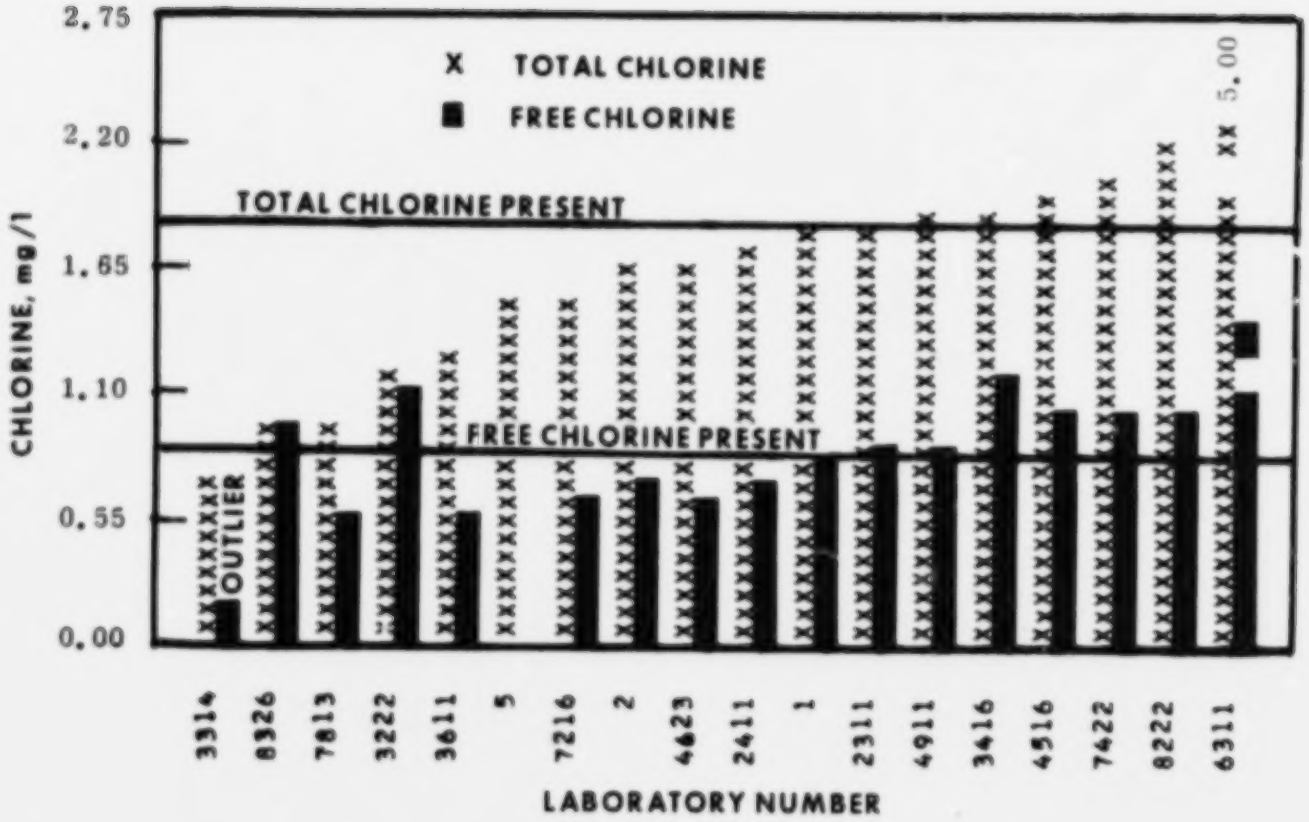

Figure 7. Bar graph for residual chlorine in sample 1 by SNORT method.

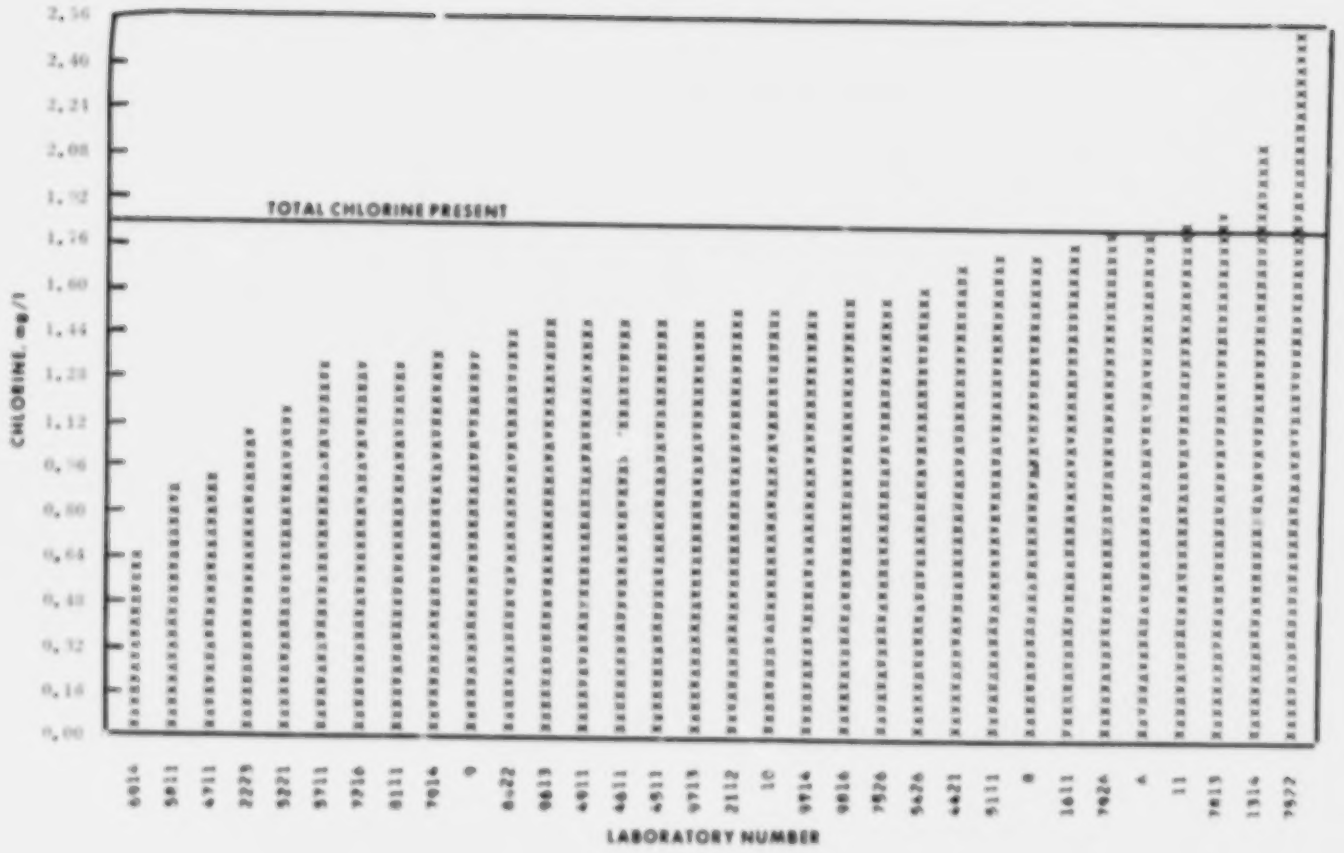

Figure 8. Bar graph for residual chlorine in sample 1 by iodometric method.

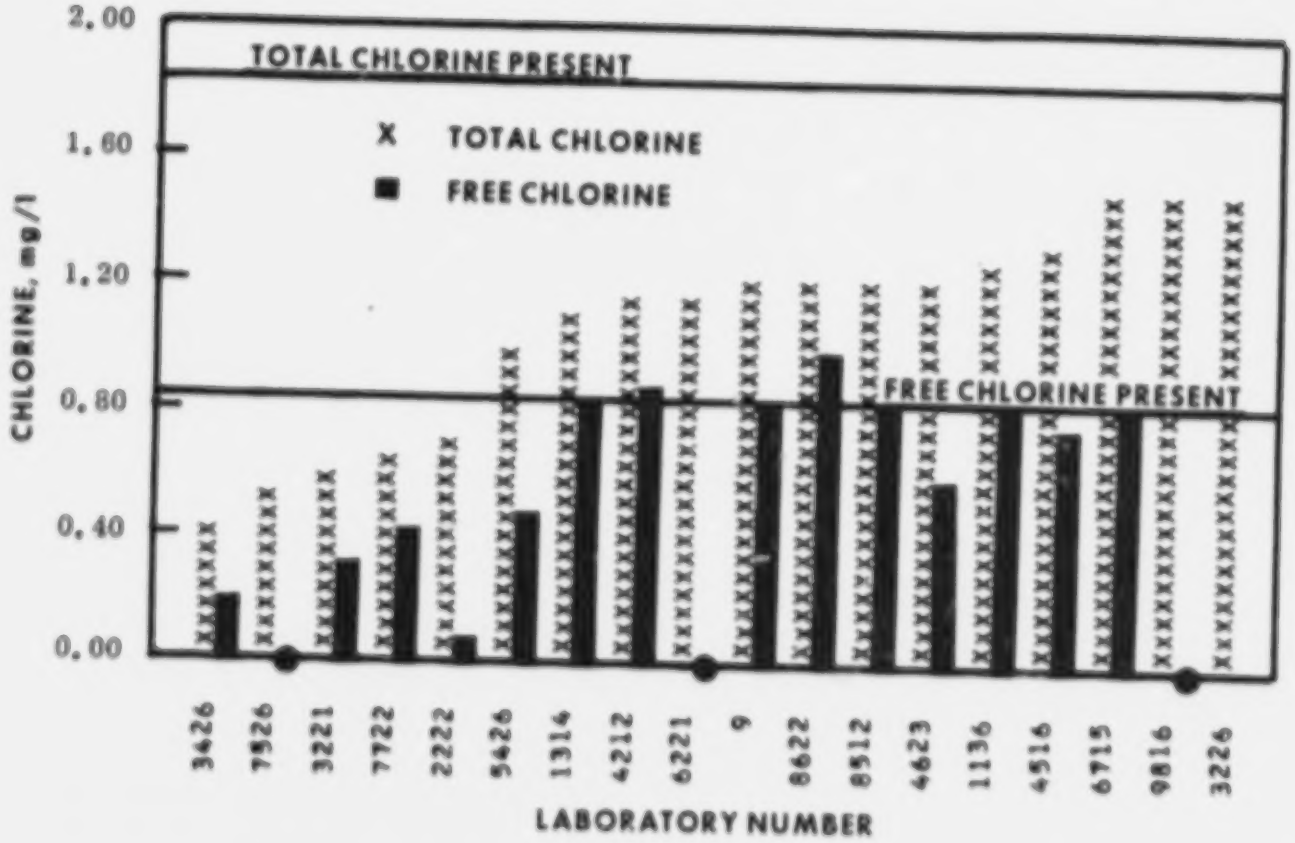

Figure 9. Bar graph for residual chlorine in sample 1 by orthotolidine method.

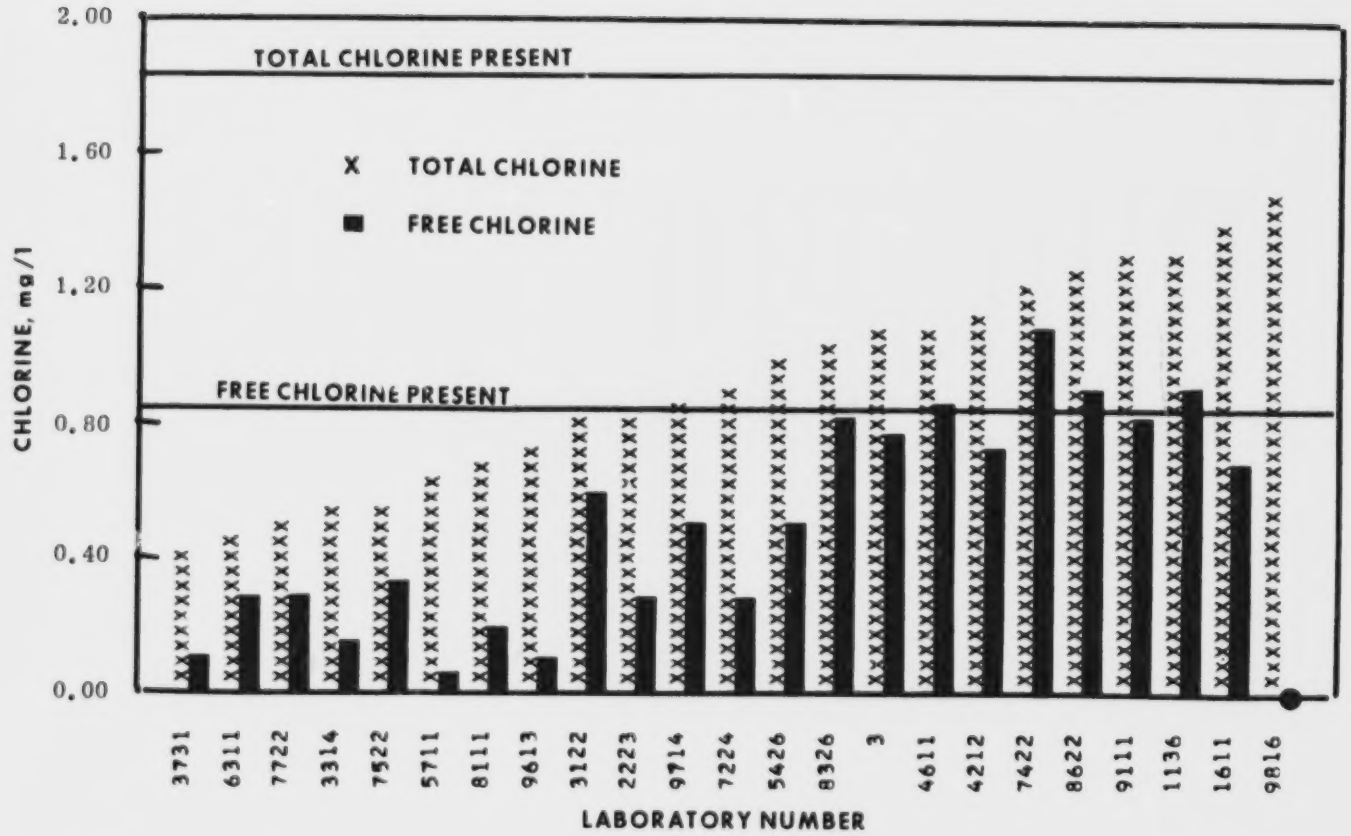

Figure 10. Bar graph for residual chlorine in sample 1 by orthotolidine-arsenite method.

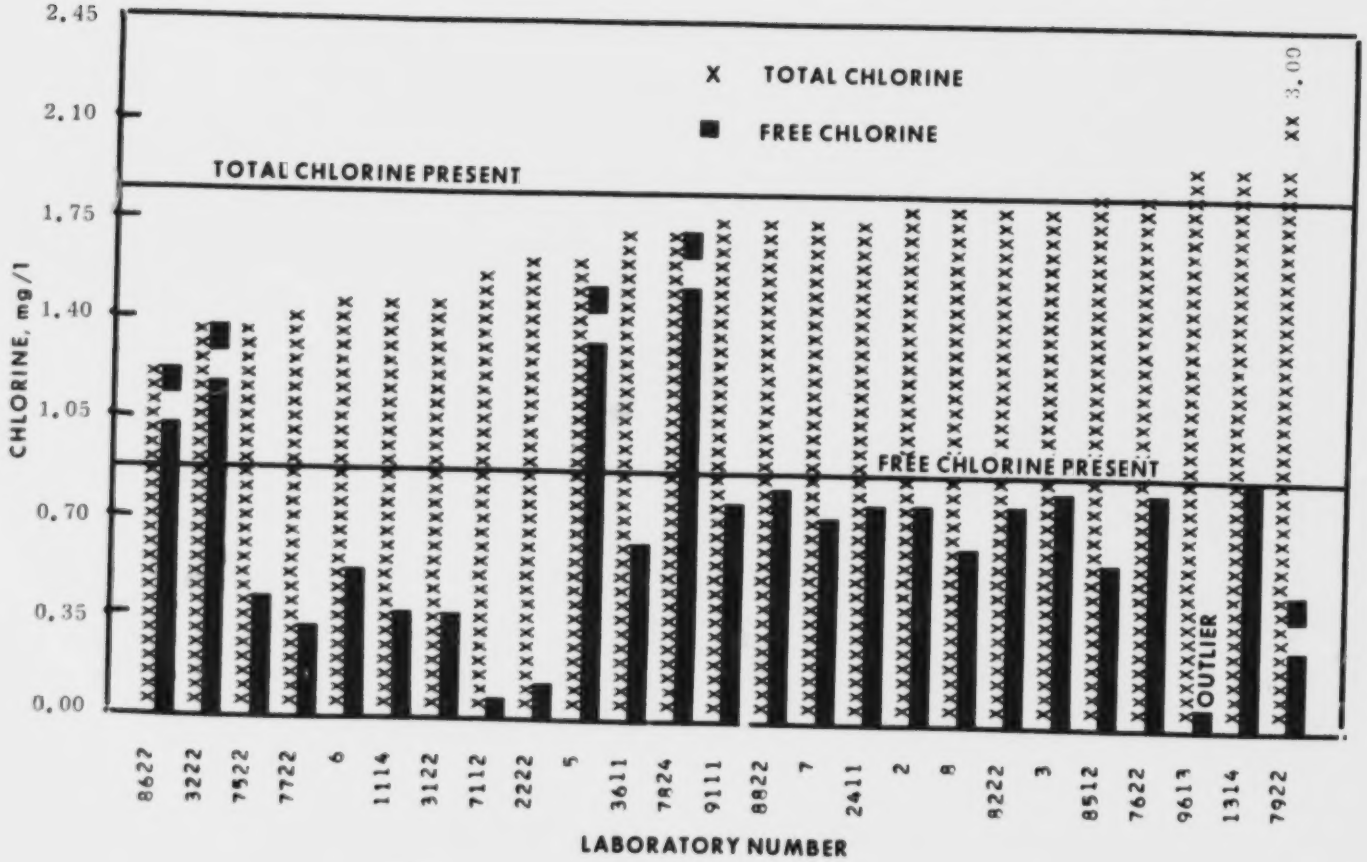

Figure 11. Bar graph for residual chlorine in sample 1 by amperometric method.

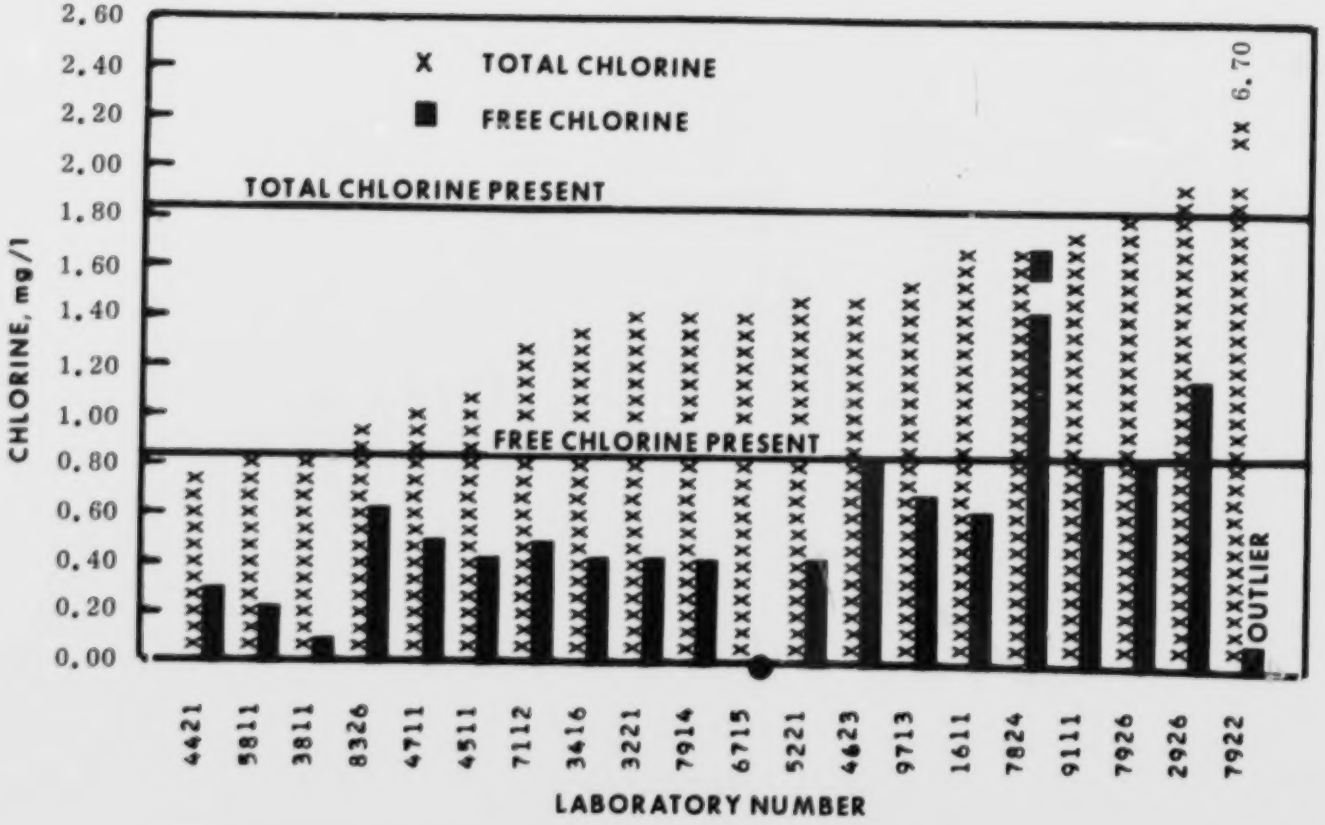

Figure 12. Bar graph for residual chlorine in sample 1 by ferrous-OT method.

Sample 2: 0.80 mg/liter free, and 0.84 mg/liter total chlorine (Table 3; Figures 13 through 21)

This sample was designed to provide only free chlorine, which was liberated from the mixture of HTH and sodium chloride when dissolved in chlorine-demand-free water. Repeated analysis by the referee laboratories, however, consistently indicated a combined-chlorine content of 0.04 mg/liter, which is an artifact due to the inability of the method to determine lesser amounts. Since the sample theoretically contained no combined chlorine, statistical analysis of the results for combined chlorine are of relatively little value. High values probably indicate contamination of the sample by absorption of ammonia from the atmosphere or the use of dilution water not free of chlorine demand. Hence, combined-chlorine results are not summarized in Table 3, but individual values appear in the tabulated data and are indicated in the bar graphs by the differences between the values for free and total chlorine (Figures 13 through 21).

In the analysis of sample 2 for free chlorine, the mean values obtained by the SNORT[4] and leuco crystal violet[2] methods were not significantly different from the referee value. The methyl orange,[1] ferrous-DPD,[3] and amperometric[8] methods appear to be nearly as accurate. There were no significant differences in the precision of any of the methods. Note, however, that considerably better precision and accuracy was shown by all methods in the determination of total chlorine, and this result arouses the suspicion of contamination of the sample by the participants.

In the determination of total chlorine in sample 2, the mean values obtained by the leuco crystal violet and methyl orange methods were not significantly different from the referee value. The amperometric, ferrous DPD, and the SNORT methods were not far behind. Again, none of the methods were significantly more precise than any of the others, but all were more precise (as noted above) in the determination of total chlorine than in the determination of free chlorine.

The least accurate results were obtained by the ferrous-OT,[9] the orthotolidine,[6] and the orthotolidine-arsenite[7] methods in the analysis for both free and total chlorine.

Table 3. SUMMARY OF DATA ON SAMPLE 2 (0.80 mg/liter free and 0.84 mg/liter total chlorine)

Method	Determination	Number of results	Number of outliers	Mean	Mean error	Standard deviation	Relative error	Relative std. dev.	95% tol. limits
Methyl orange	Free	26	2	0.624	-0.176	0.268	22.0	43.0	0.701
	Total	26	2	0.794	-0.047	0.188	5.5	23.7	0.490
Leuco crystal violet	Free	17	1	0.743	-0.057	0.243	7.1	32.7	0.694
	Total	17	1	0.816	-0.024	0.204	2.8	25.0	0.582
Ferrous-DPD	Free	19	1	0.642	-0.158	0.255	19.8	39.8	0.711
	Total	19	1	0.725	-0.115	0.222	13.7	30.6	0.618
SNORT	Free	15	2	0.698	-0.102	0.243	12.8	34.7	0.719
	Total	15	3	0.721	-0.119	0.197	14.2	27.3	0.582
Iodometric	Total	32	0	0.642	-0.198	0.174	23.6	27.0	0.438
Orthotolidine	Free	15	2	0.460	-0.340	0.297	42.5	64.6	0.878
	Total	15	3	0.625	-0.215	0.212	25.6	33.9	0.625
Orthotolidine-arsenite	Free	20	3	0.462	-0.339	0.242	42.3	52.4	0.666
	Total	20	3	0.654	-0.186	0.147	22.1	22.5	0.405
Amperometric	Free	23	2	0.600	-0.200	0.254	25.0	42.3	0.679
	Total	23	2	0.761	-0.079	0.174	9.4	22.9	0.466
Ferrous-OT	Free	19	1	0.468	-0.332	0.247	41.4	52.6	0.686
	Total	19	1	0.602	-0.238	0.202	28.4	33.6	0.563

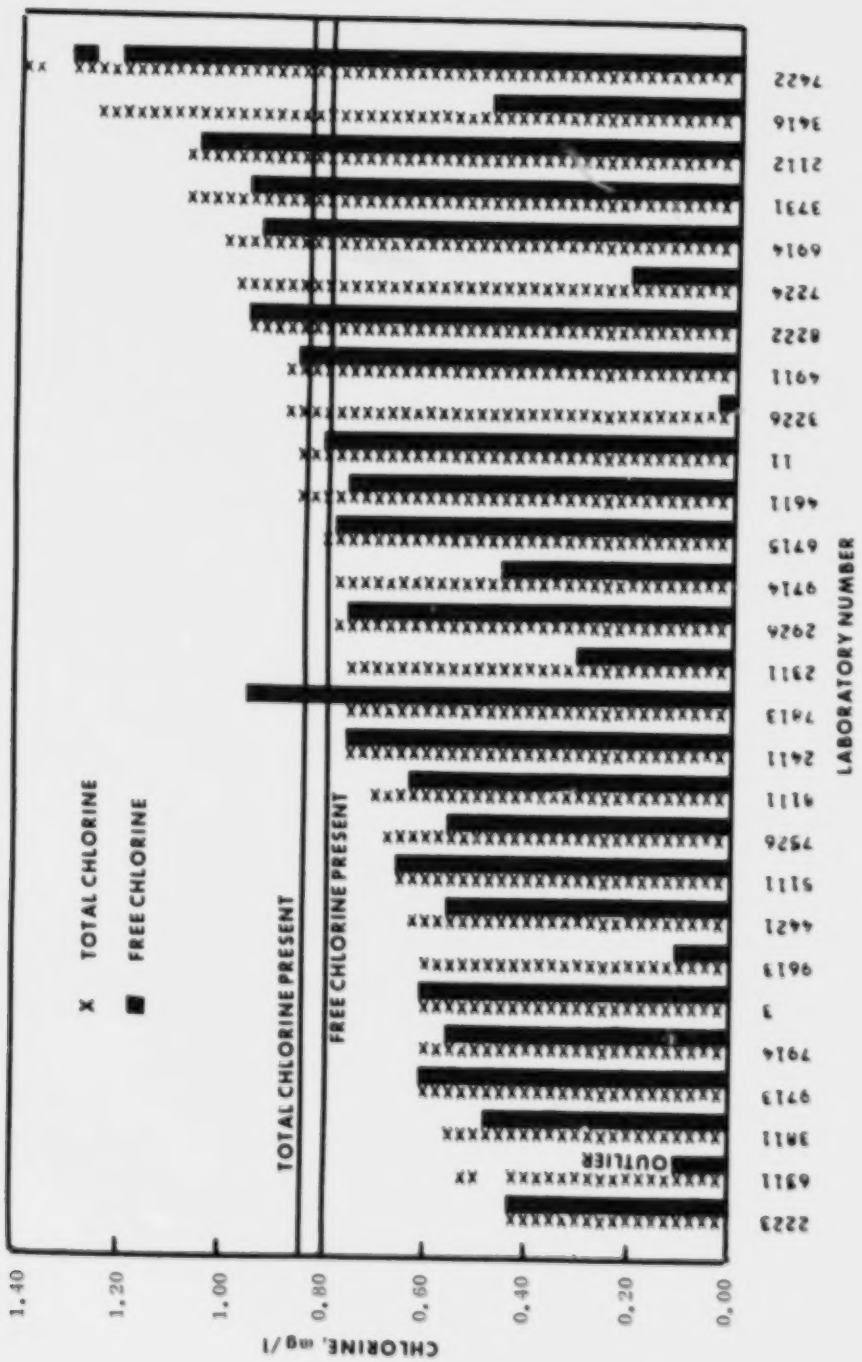

Figure 13. Bar graph for residual chlorine in sample 2 by methyl orange method.

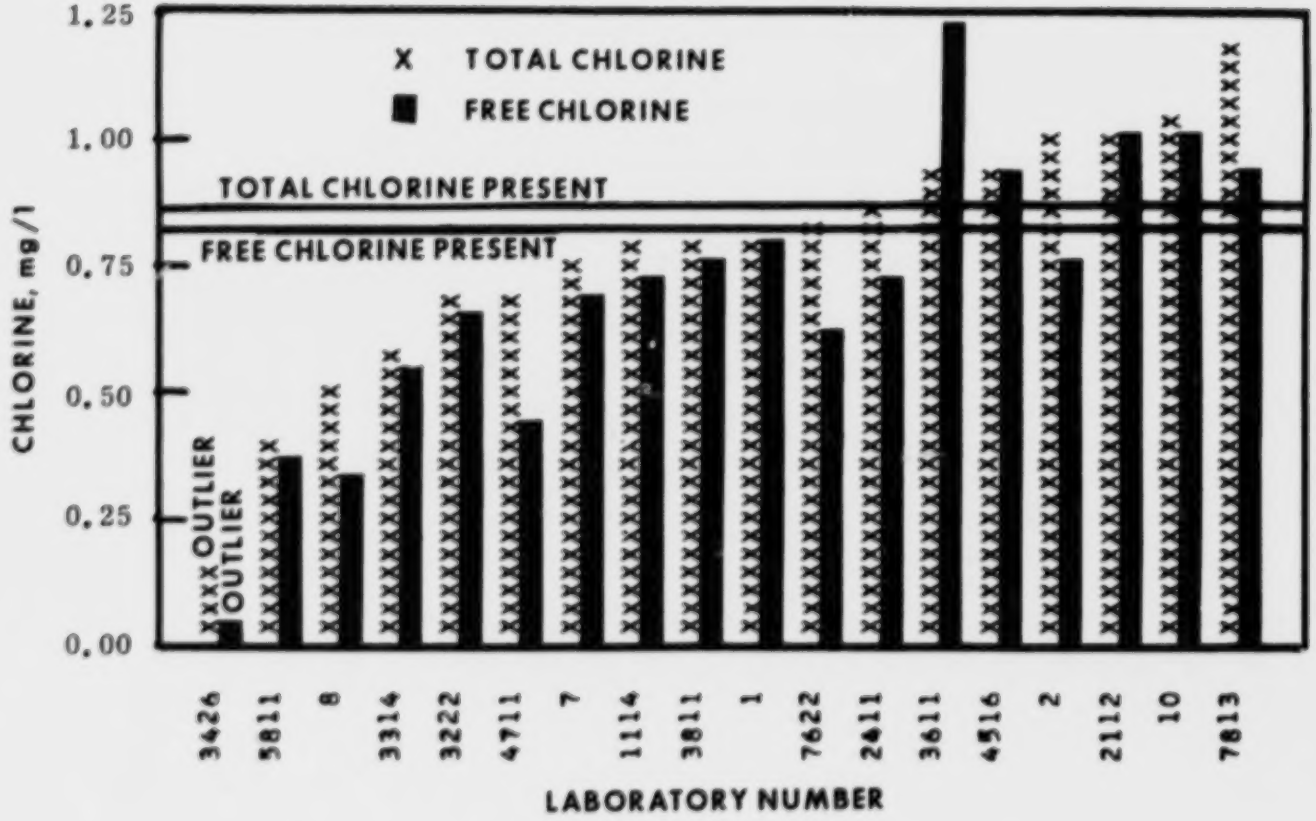

Figure 14. Bar graph for residual chlorine in sample 2 by leuco crystal violet method.

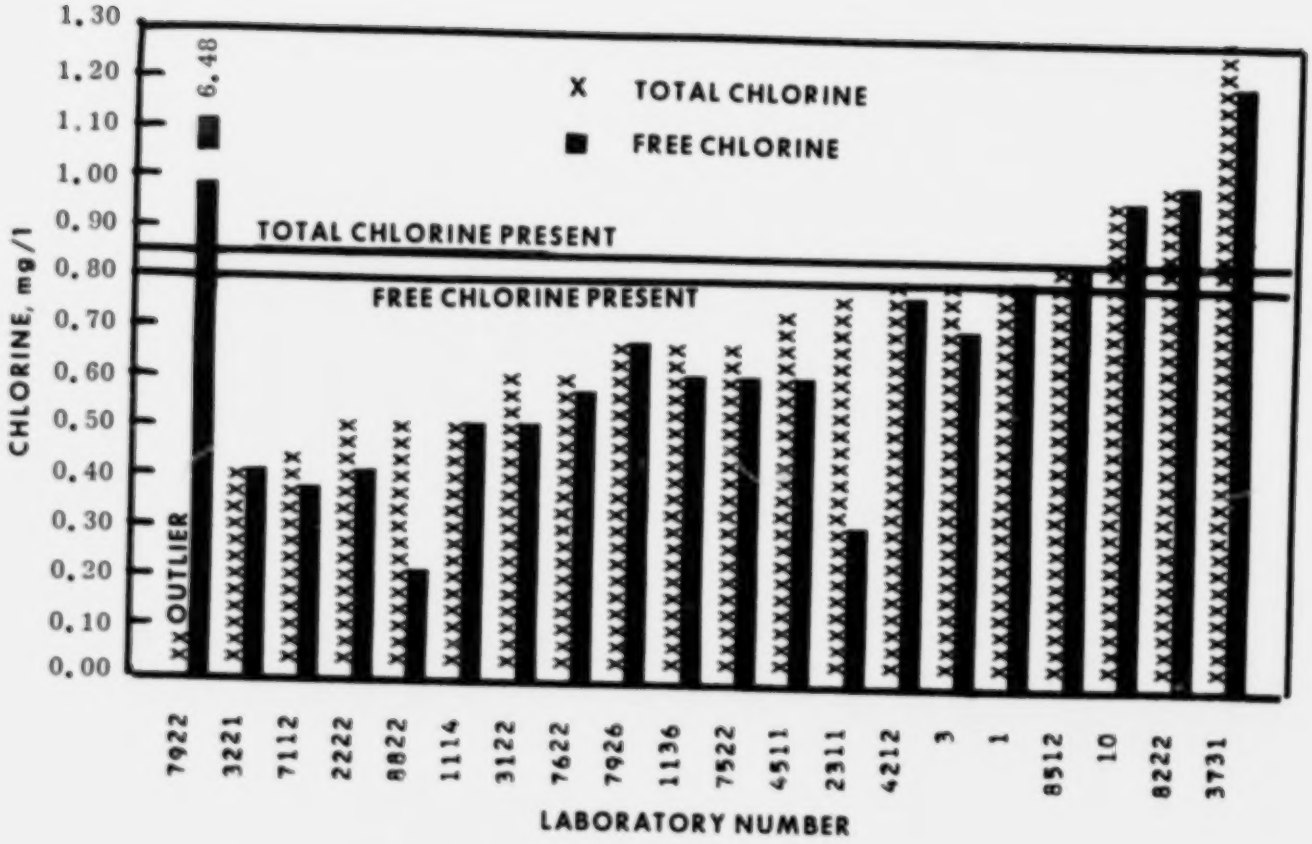

Figure 15. Bar graph for residual chlorine in sample 2 by ferrous-DPD method.

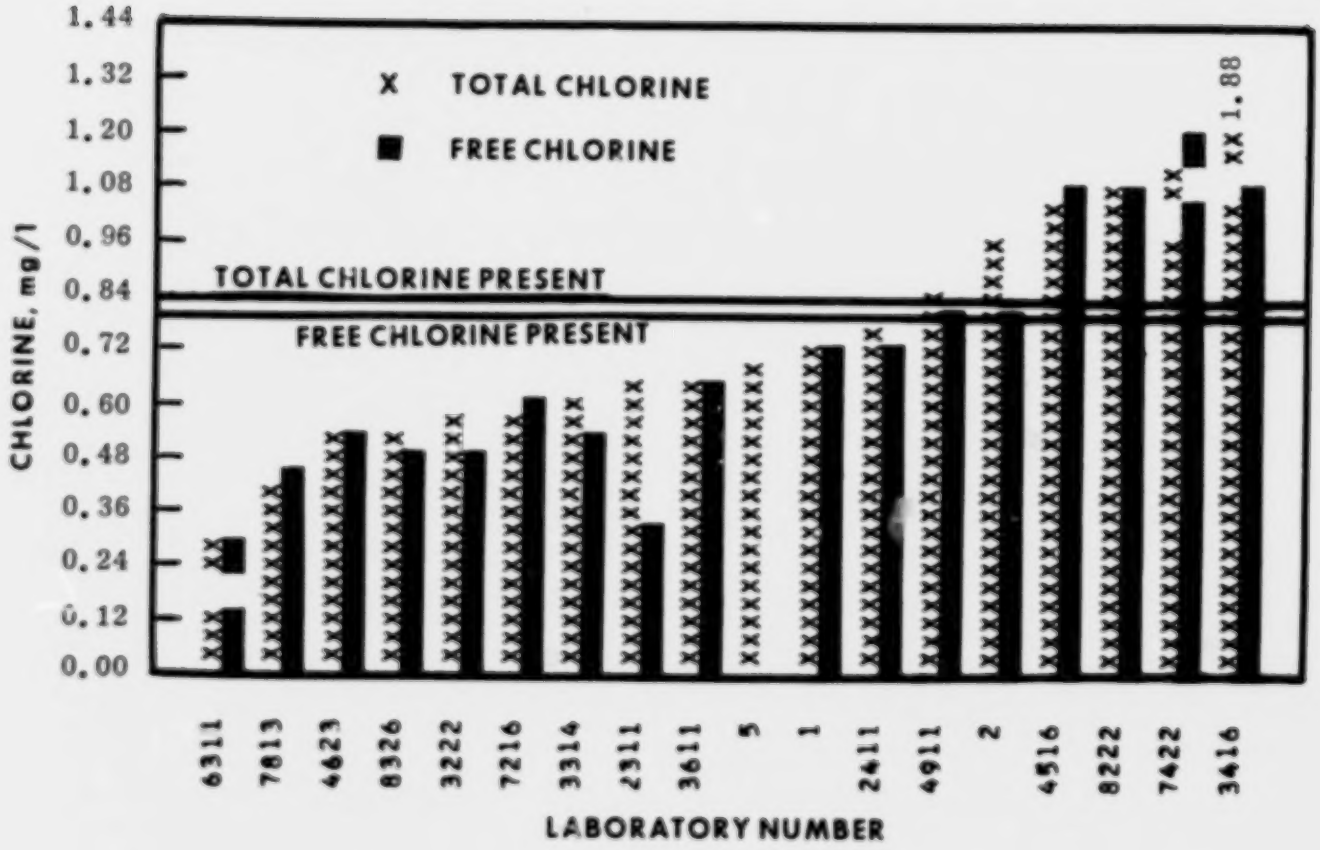

Figure 16. Bar graph for residual chlorine in sample 2 by SNORT method.

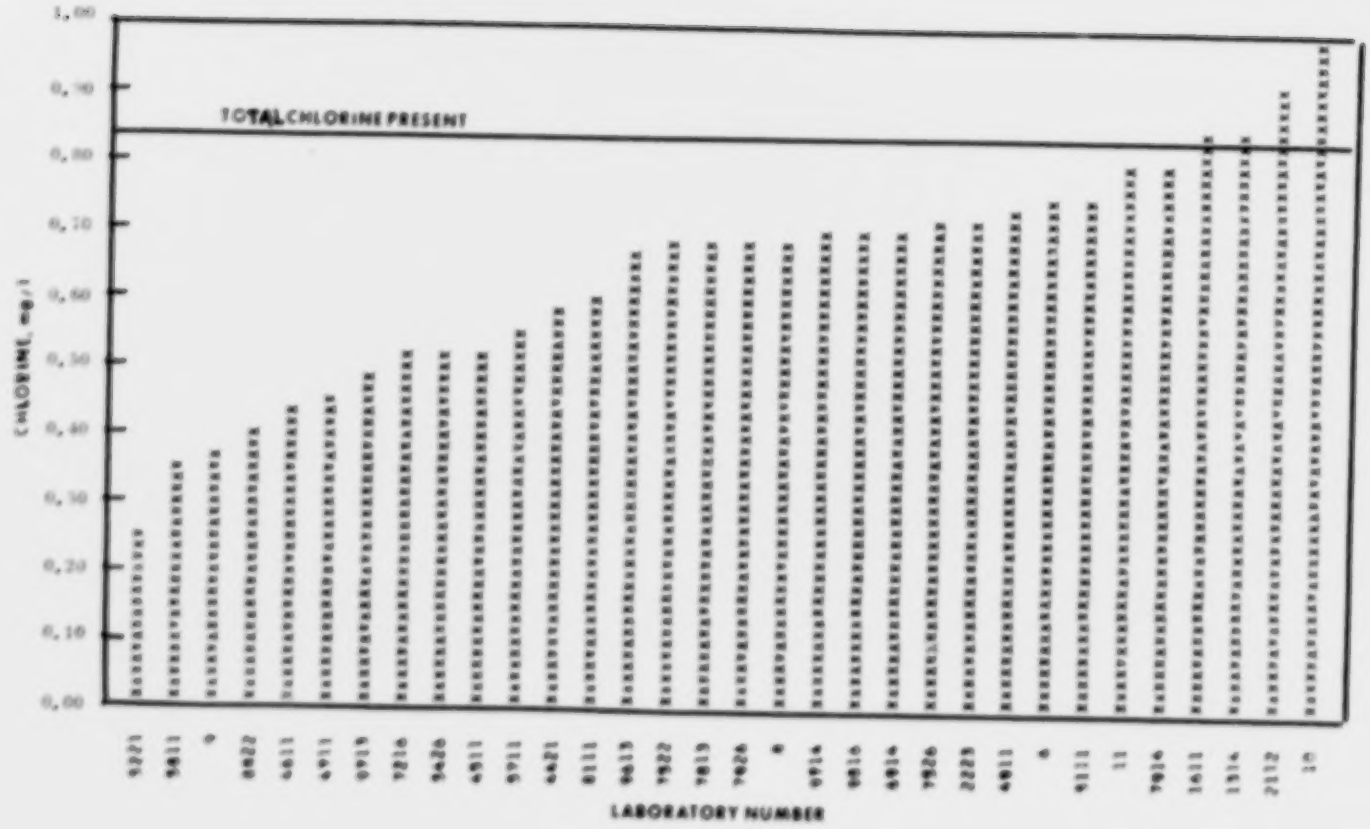

Figure 17. Bar graph for residual chlorine in sample 2 by iodometric method.

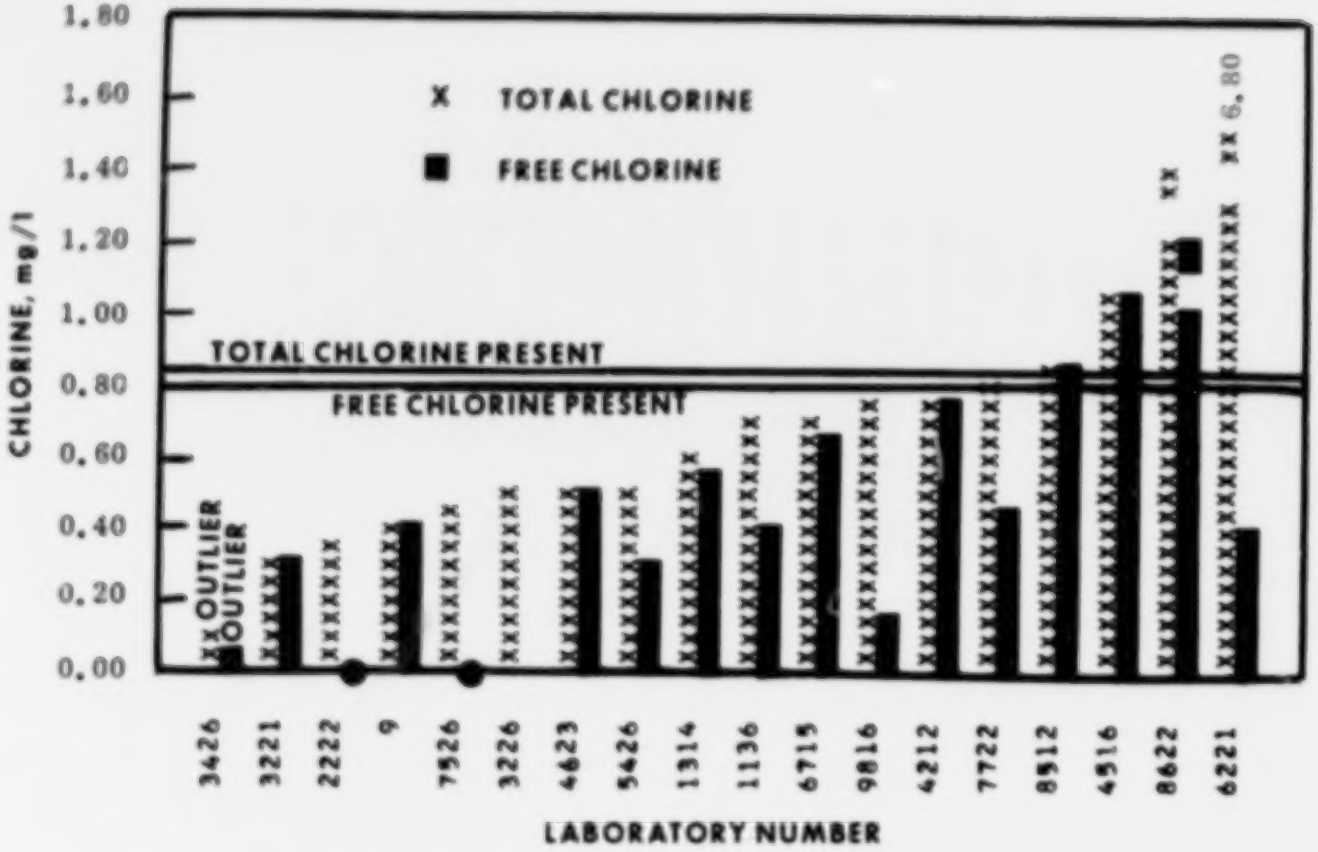

Figure 18. Bar graph for residual chlorine in sample 2 by orthotolidine method.

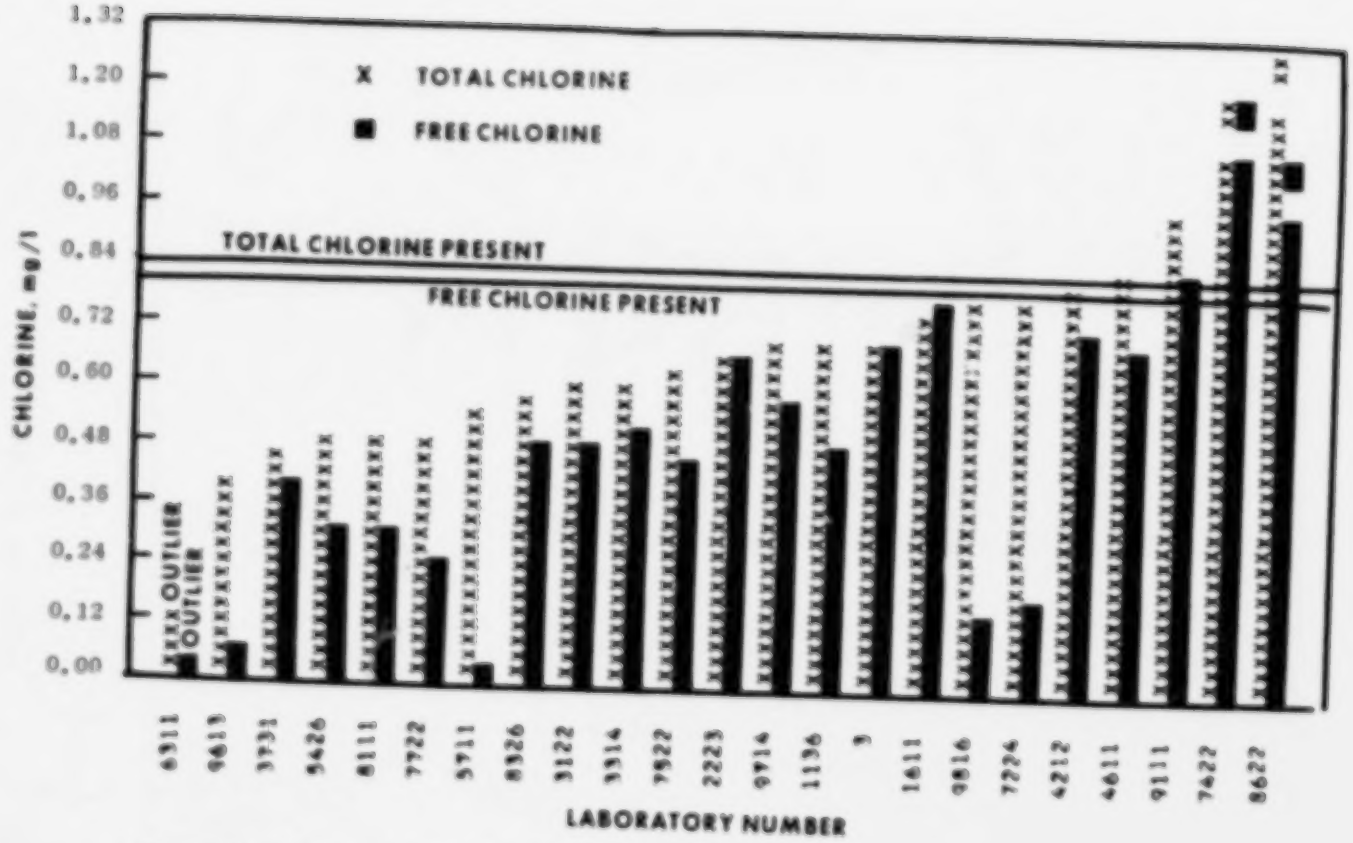

Figure 19. Bar graph for residual chlorine in sample 2 by orthotolidine-arsenite method.

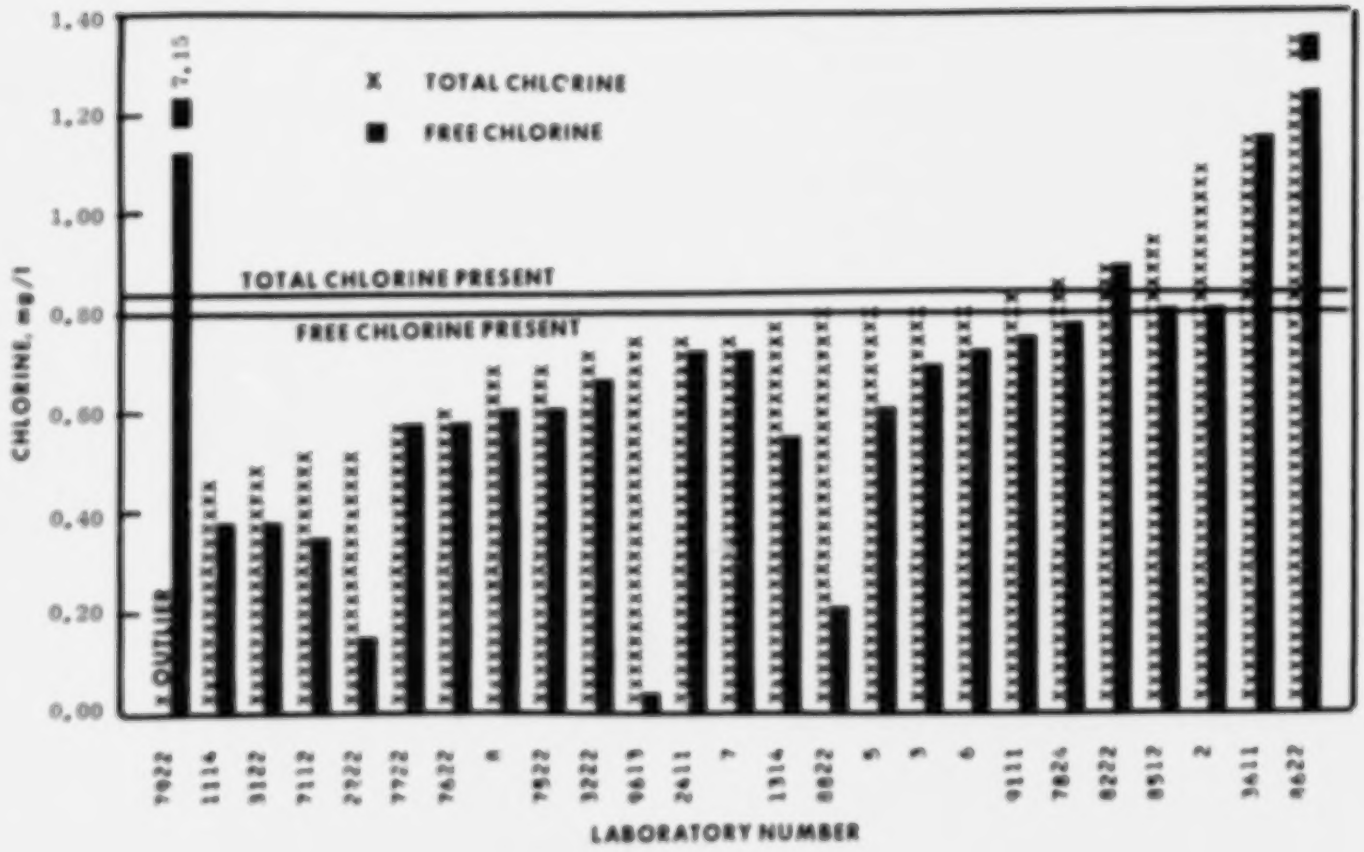

Figure 20. Bar graph for residual chlorine in sample 2 by amperometric method.

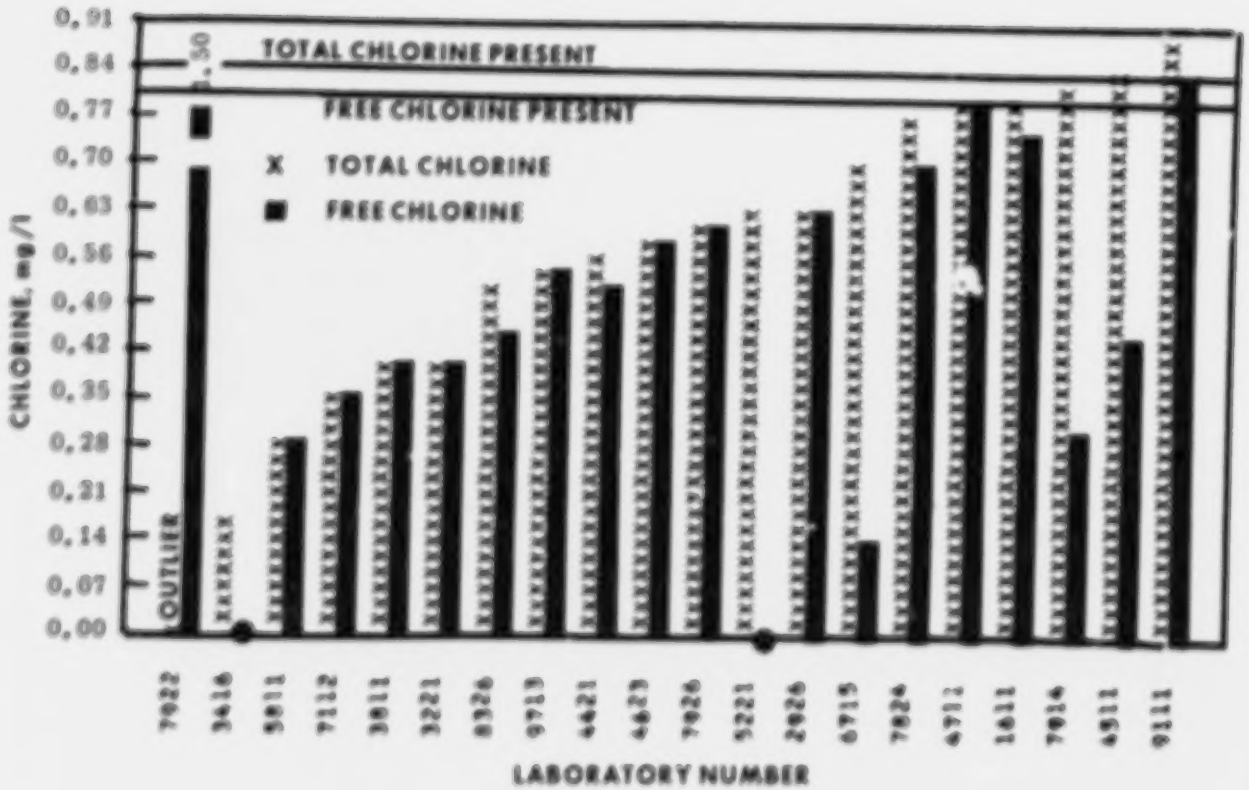

Figure 21. Bar graph for residual chlorine in sample 2 by ferrous-OT method.

Sample 3: 0.60 mg/liter combined, and 0.64 mg/liter total chlorine (Table 4; Figures 22 through 30)

This sample was designed to provide only combined chlorine by using a mixture of HTH and sodium chloride, similar to sample 2, and adding a specified amount of ammonia chloride-borate buffer solution after dissolving the mixture in chlorine demand-free water. Repeated analysis by referee laboratories indicated an average free-chlorine content of 0.04 mg/liter, but as in the measurement of combined chlorine in sample 2, this is an artifact due to the inability of the method to determine lesser amounts. Statistical analysis of the free-chlorine results is, therefore, of little value and is not reported in Table 4, but the individual values can be found in the tabulated data and are plotted on the bar graphs (Figures 22 through 30).

In the analysis of sample 3 for combined chlorine, the mean values obtained by the SNORT,[4] ferrous-DPD,[3] methyl orange,[1] and the leuco crystal violet[2] methods were not significantly different from the referee value. The ferrous-DPD[3] was significantly more precise than the other methods.

In the analysis of sample 3 for total chlorine, the mean values obtained by the leuco crystal violet, SNORT, ferrous DPD, and the amperometric[8] methods were not significantly different from the referee value, and the precision of the ferrous-DPD method was significantly better than that of all the others.

Note that, while the amperometer gave very accurate results for total chlorine, high values were obtained for free chlorine, and this result caused the calculated combined chlorine to be low. It is very likely that the high free-chlorine values were caused by the incomplete rinsing of the amperometer electrode after the determination of total chlorine.

Table 4. SUMMARY OF DATA ON SAMPLE 3 (0.60 mg/liter combined and 0.64 mg/liter total chlorine)

Method	Determination	Number of results	Number of outliers	Mean	Mean error	Standard deviation	Relative error	Relative std. dev.	95% tol. limits
Methyl orange	Combined	26	2	0.572	-0.028	0.224	4.7	39.2	0.585
	Total	26	2	0.731	+0.091	0.220	14.2	30.1	0.575
Leuco crystal violet	Combined	17	1	0.566	-0.034	0.172	5.7	30.5	0.493
	Total	17	1	0.646	-0.006	0.222	0.9	34.4	0.636
Ferrous-DPD	Combined	17	2	0.587	-0.013	0.120	2.2	20.4	0.342
	Total	19	1	0.588	-0.052	0.113	8.1	19.2	0.314
SNORT	Combined	15	2	0.589	-0.011	0.266	1.9	45.2	0.786
	Total	16	2	0.628	-0.013	0.238	2.0	8.0	0.692
Iodometric	Total	30	3	0.522	-0.118	0.169	18.5	32.4	0.439
Orthotolidine	Combined	14	0	0.450	-0.150	0.174	25.0	38.6	-----
	Total	17	0	0.511	-0.129	0.190	20.2	37.3	0.544
Orthotolidine-arsenite	Combined	20	1	0.446	-0.155	0.198	25.8	44.5	0.546
	Total	21	2	0.549	-0.091	0.154	14.2	28.0	0.419
Amperometric	Combined	24	1	0.494	-0.106	0.214	17.7	43.3	0.567
	Total	24	1	0.585	-0.055	0.145	8.5	24.8	0.385
Ferrous-OT	Combined	16	2	0.459	-0.141	0.120	23.5	26.1	0.347
	Total	18	2	0.476	-0.164	0.123	25.6	25.8	0.347

----- Tolerance limits were not calculated since the data is non-normal.

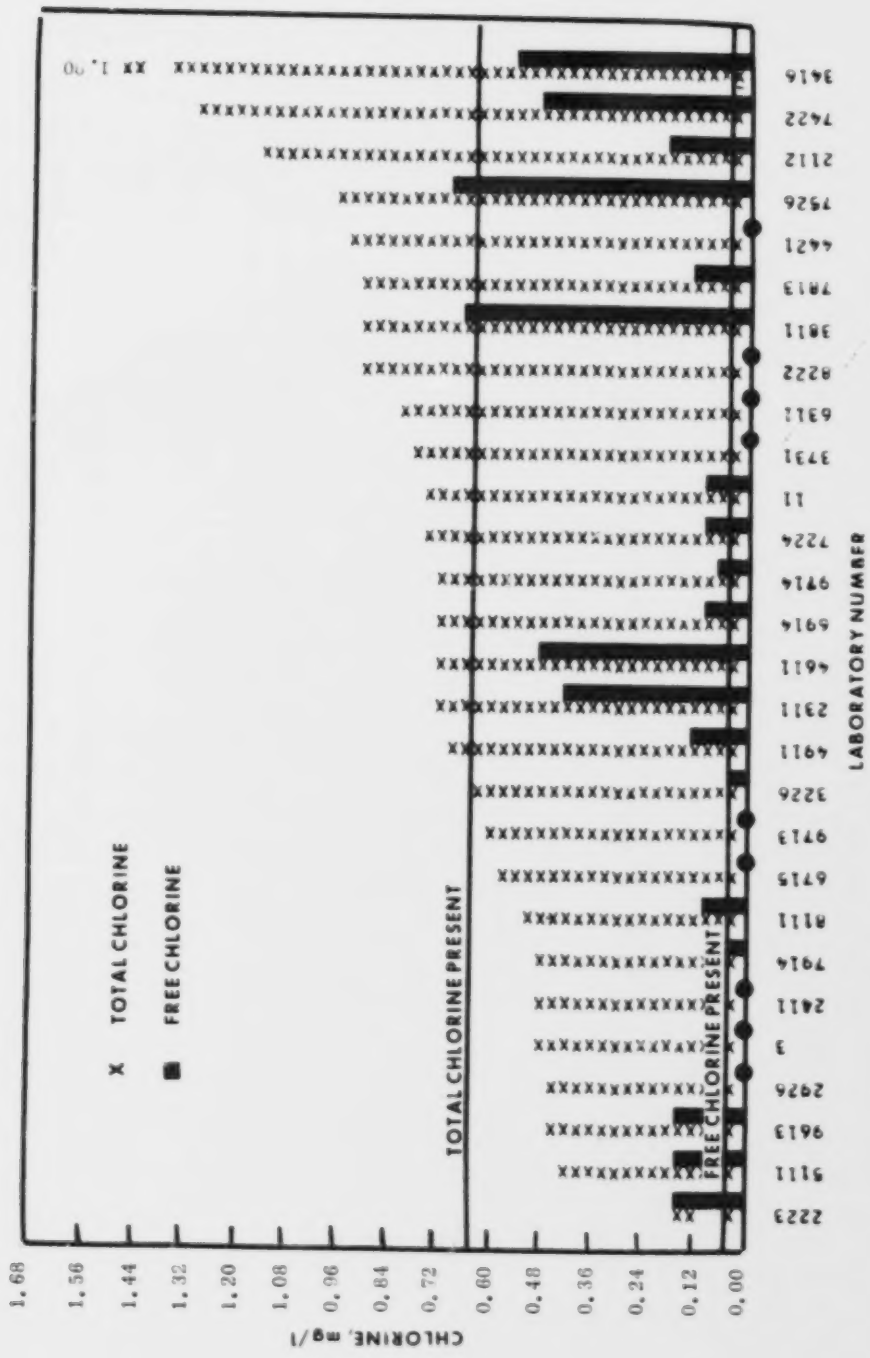

Figure 22. Bar graph for residual chlorine in sample 3 by methyl orange method.

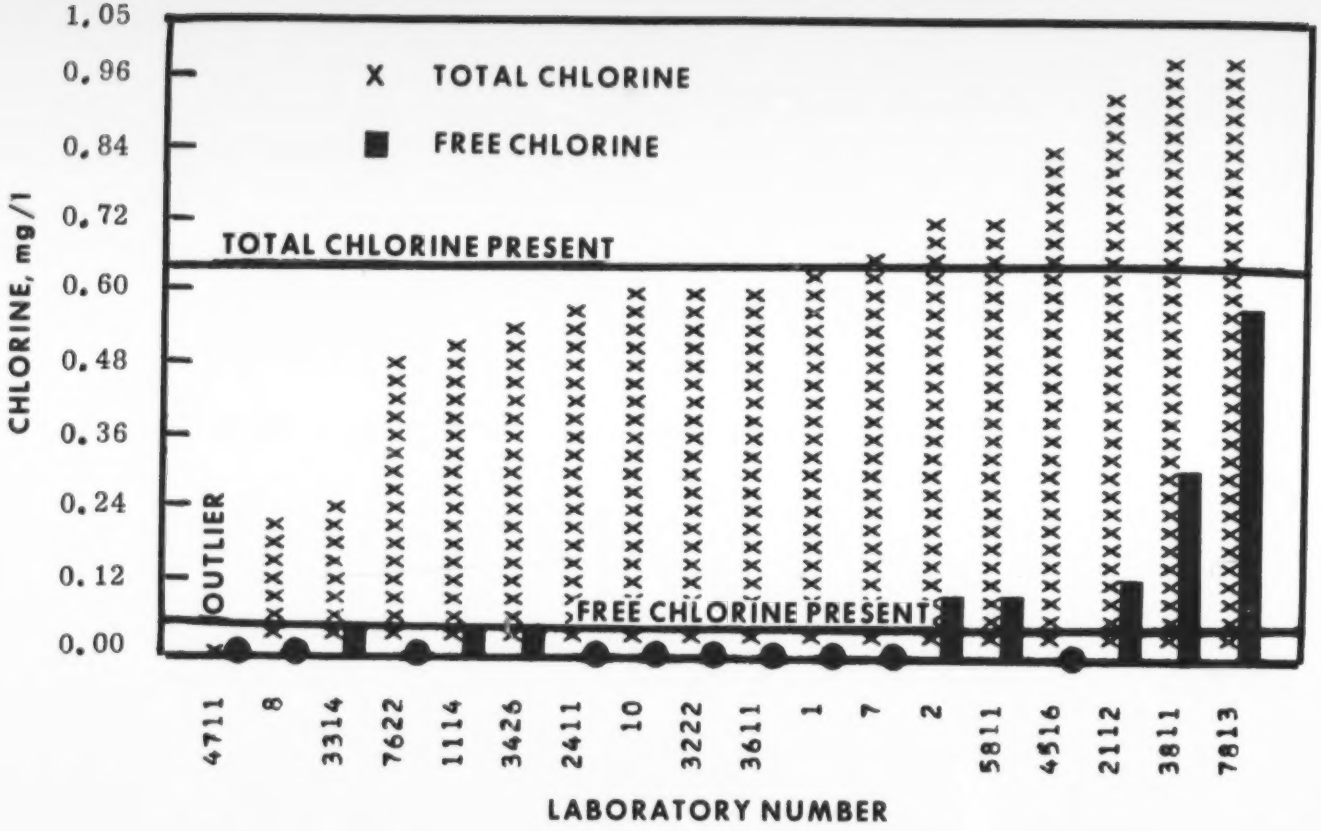

Figure 23. Bar graph for residual chlorine in sample 3 by leuco crystal violet method.

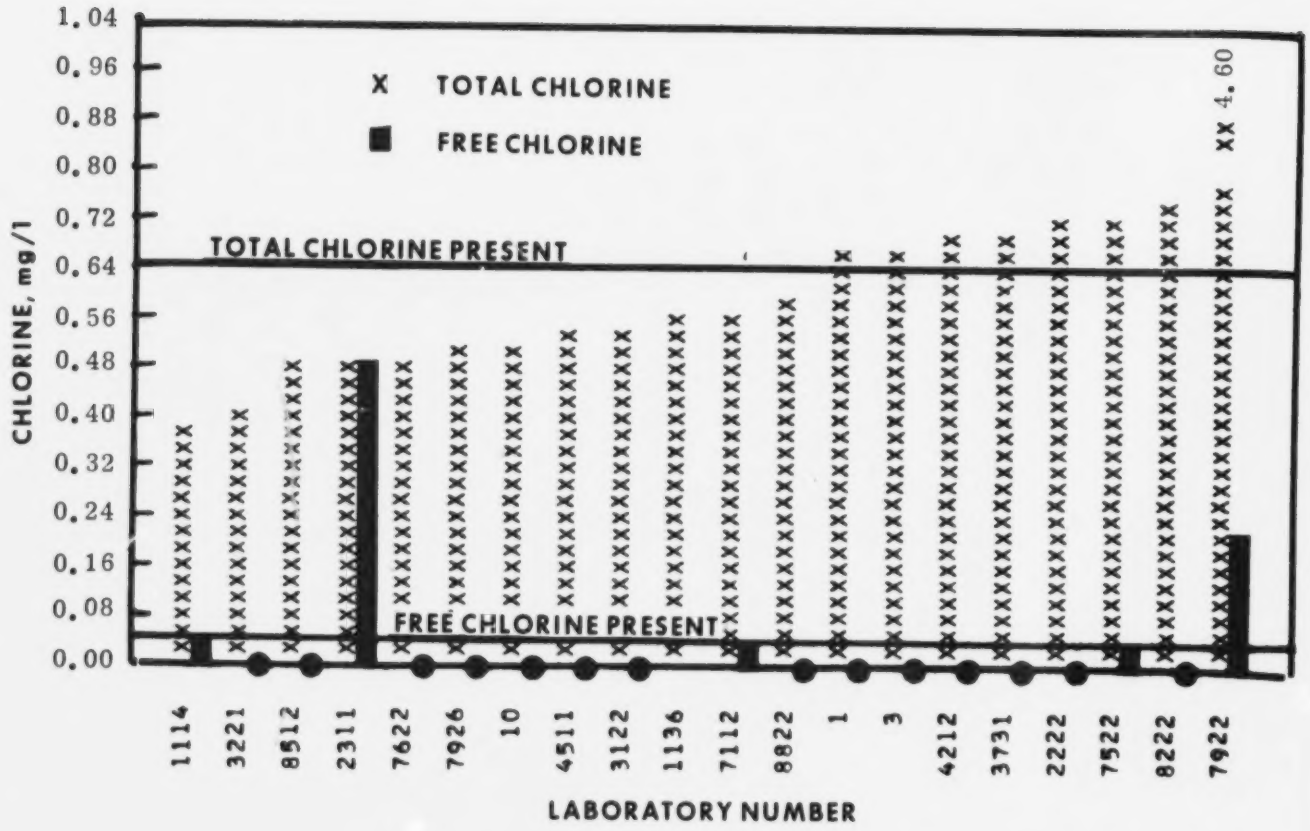

Figure 24. Bar graph for residual chlorine in sample 3 by ferrous-DPD method.

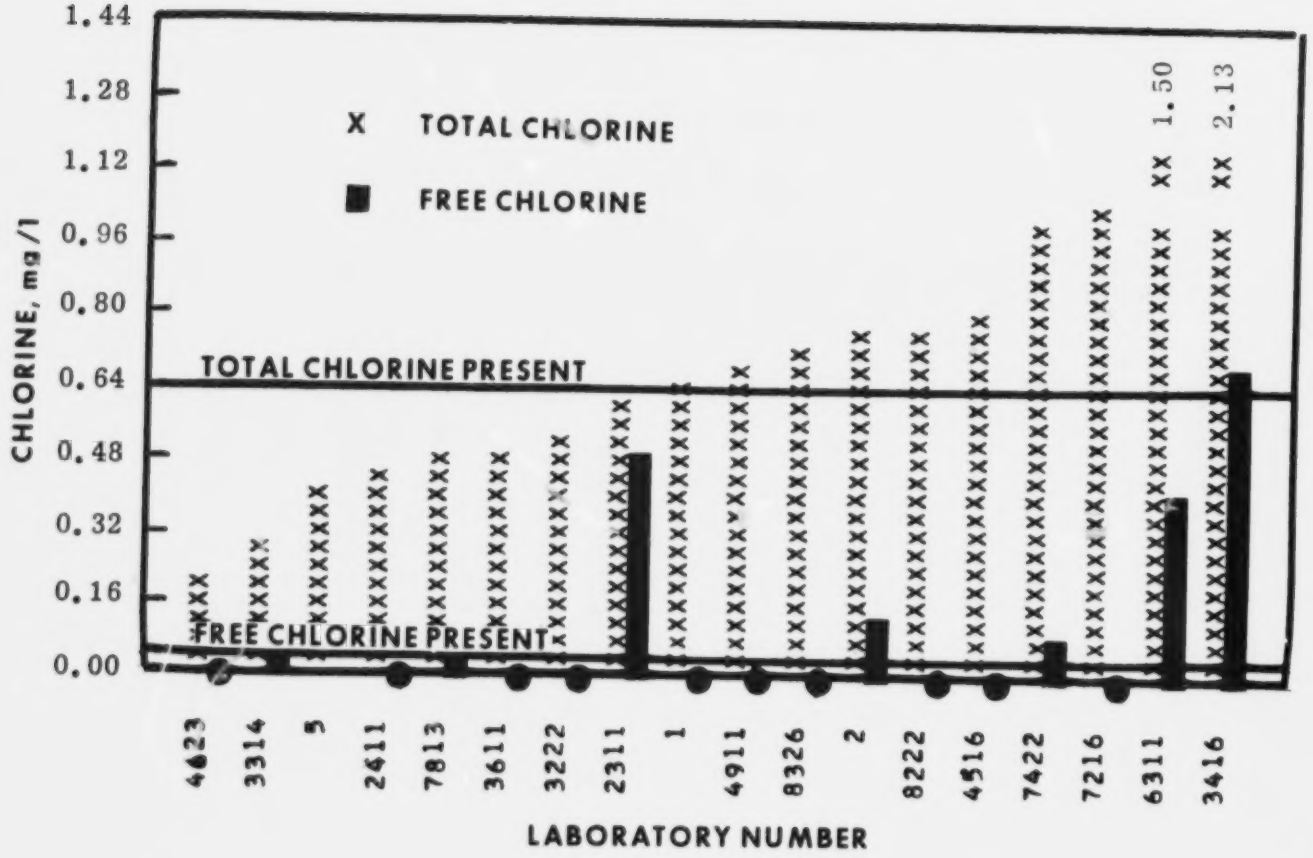

Figure 25. Bar graph for residual chlorine in sample 3 by SNORT method.

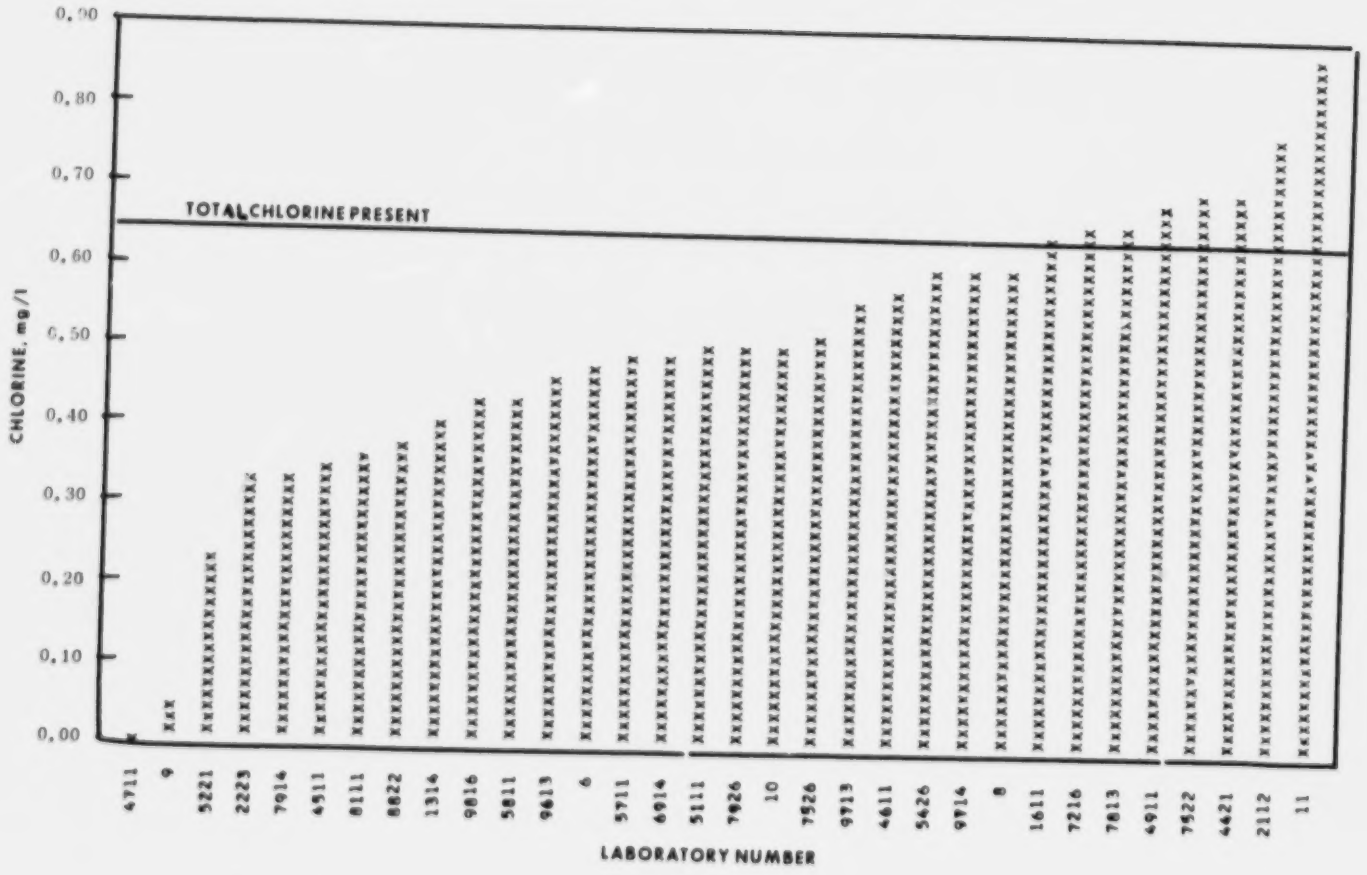

Figure 26. Bar graph for residual chlorine in sample 3 by iodometric method.

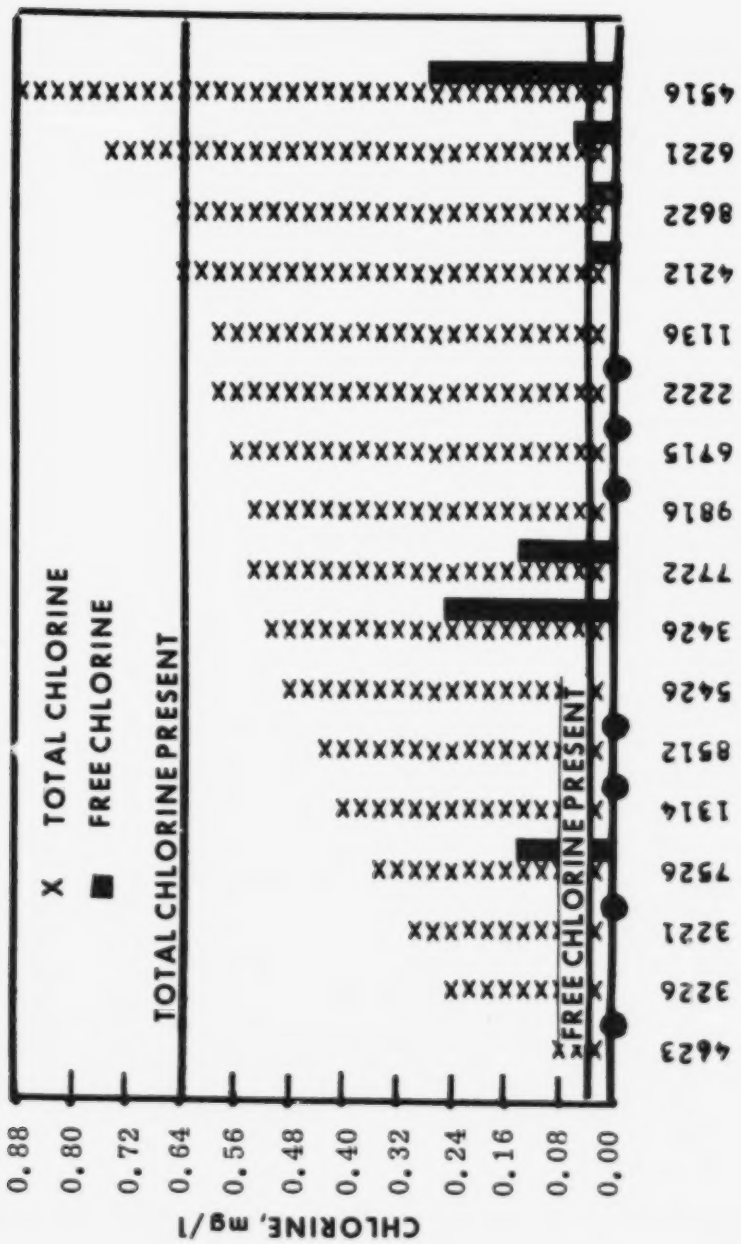

Figure 27. Bar graph for residual chlorine in sample 3 by orthotolidine method.

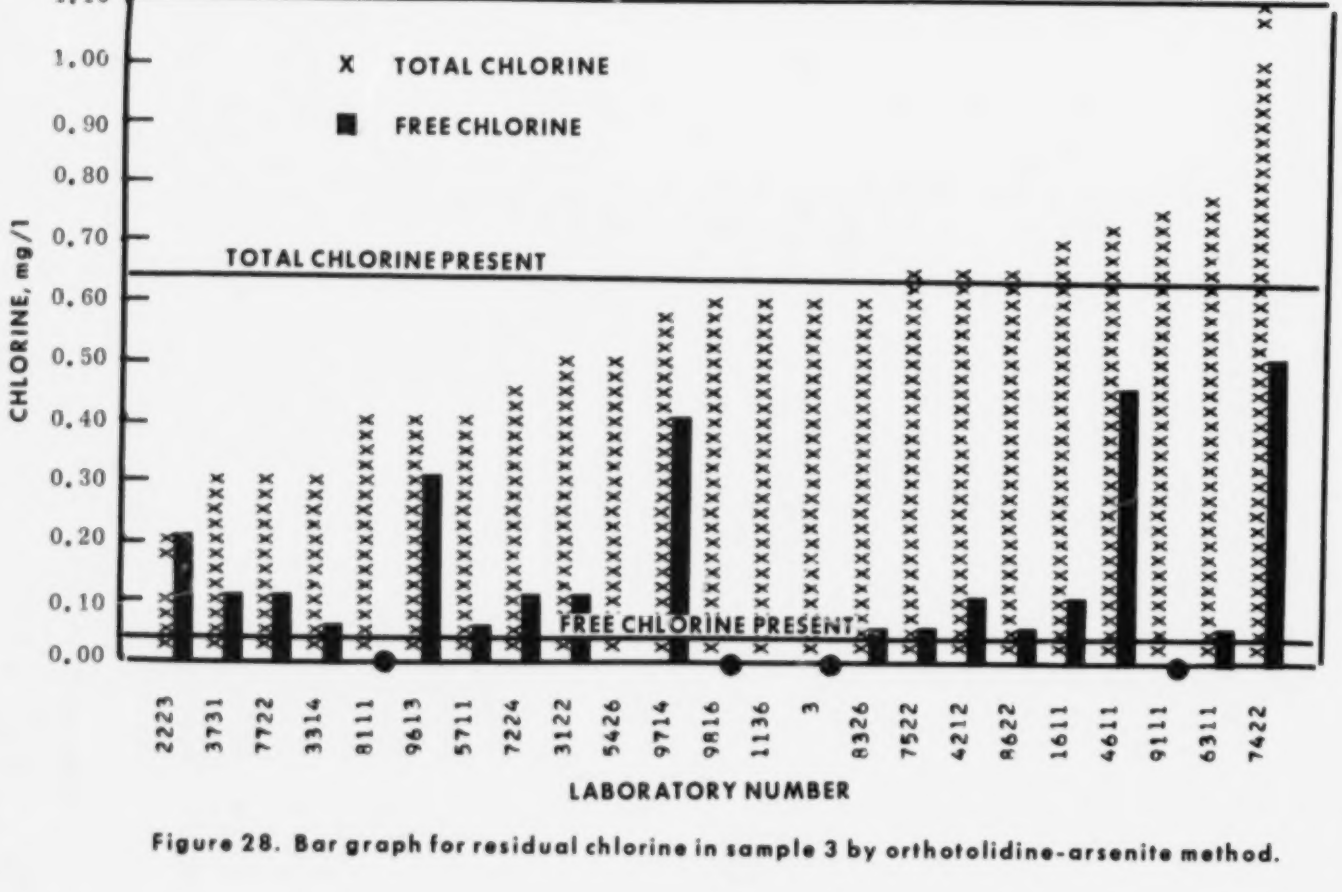

Figure 28. Bar graph for residual chlorine in sample 3 by orthotolidine-arsenite method.

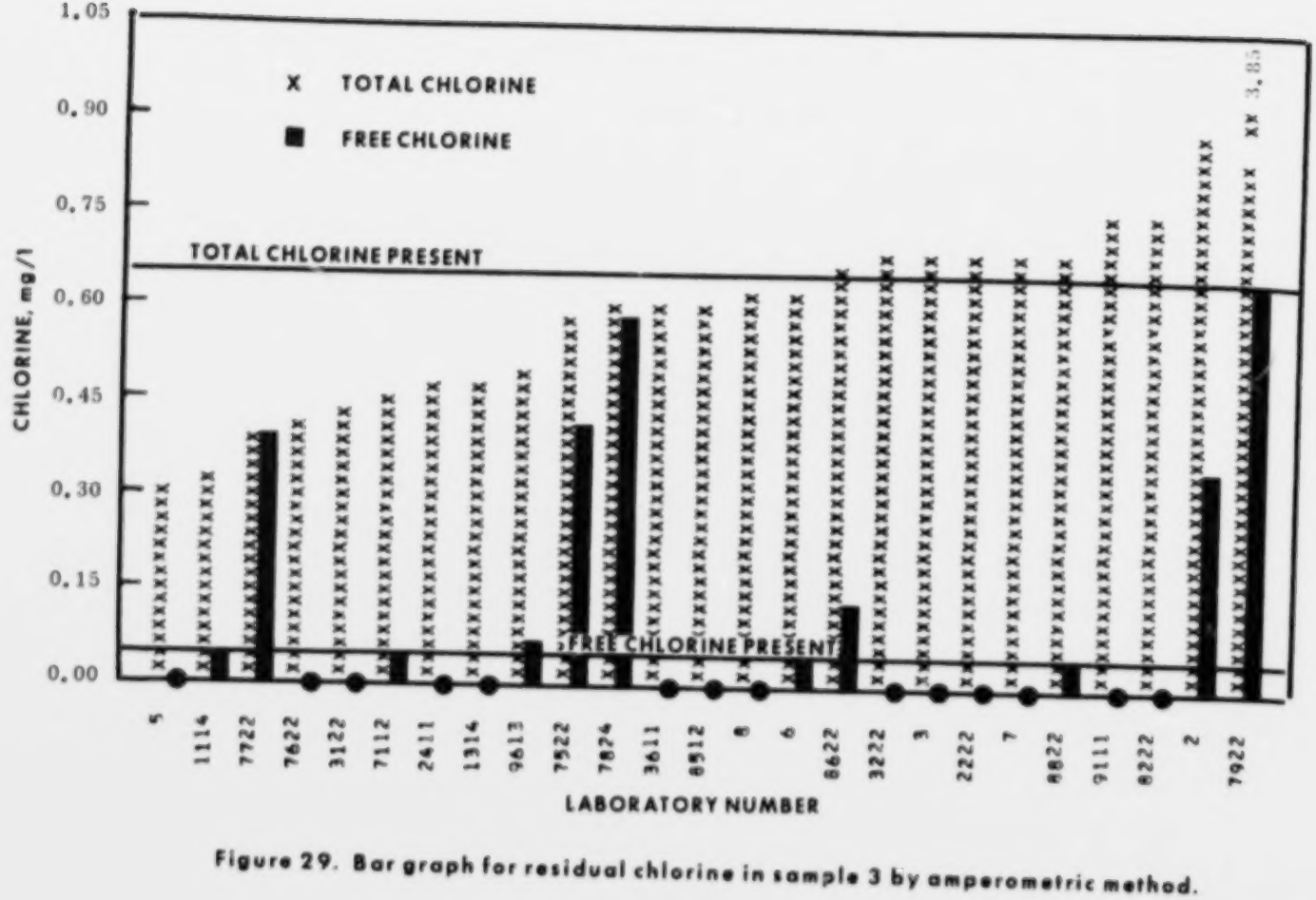

Figure 29. Bar graph for residual chlorine in sample 3 by amperometric method.

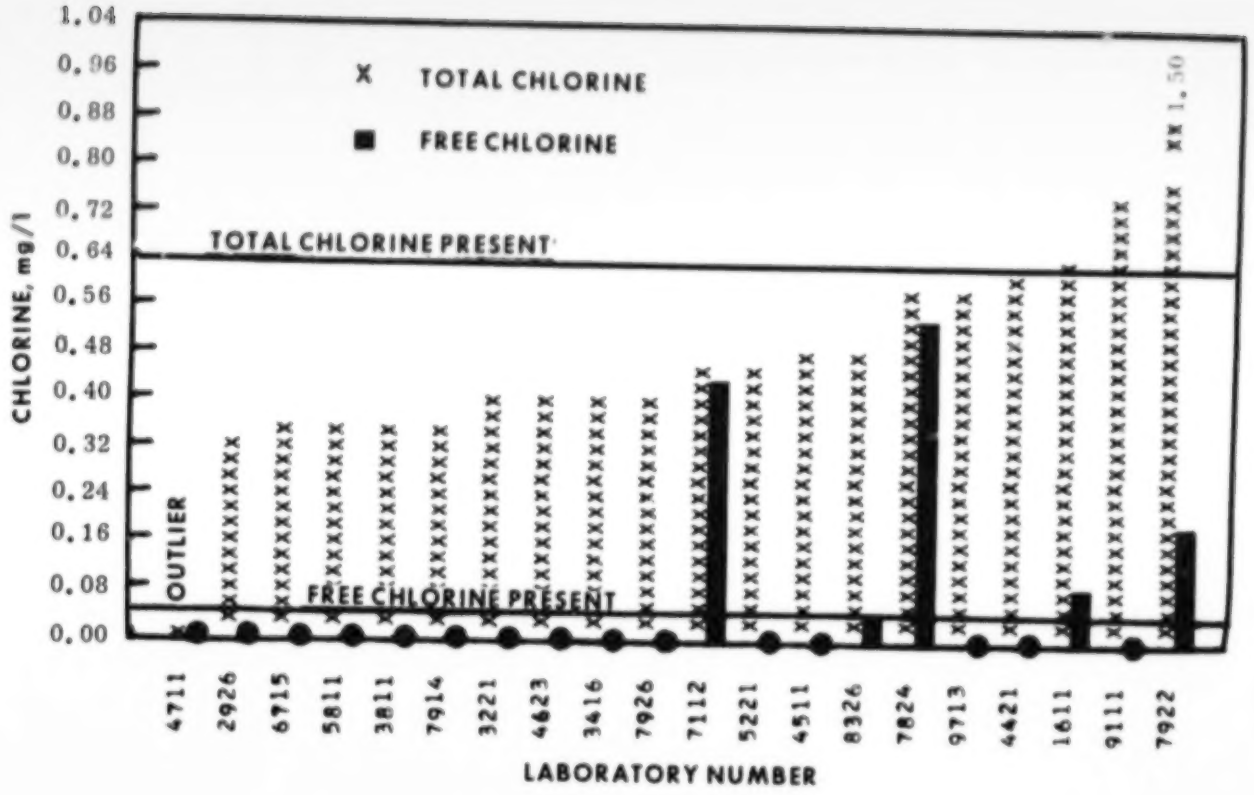

Figure 30. Bar graph for residual chlorine in sample 3 by ferrous-OT method.

DISCUSSION

The dry powder mixtures used in this study were quite stable, and hence, little variation of the samples because of decomposition was expected. It was realized, however, that because the dry powders were mixtures of several chemicals (to achieve stability) some variation between aliquots might be expected. It was hoped, moreover, that, by requiring each laboratory to analyze the samples by three different methods, any difference between the methods would become evident, even though their precision would be poor. This objective has apparently been accomplished, though recent investigations in the ARS laboratory have shown that a chlorine solution sealed in a glass ampoule and stored in the dark (at room temperature) will remain stable for at least 3 months and probably longer. This would appear to be a better way of preparing chlorine samples for use in future studies.

In the measurement of free chlorine in sample 1, the leuco crystal violet method produced the poorest results. On the other hand, in the analysis of sample 2 for free chlorine this procedure produced the best accuracy and precision. Likewise, in the analysis of sample 3 for combined chlorine, while the precision of the method was not as good as the ferrous-DPD method, there was no significant difference in accuracy. Apparently, the leuco crystal violet procedure is capable of inhibiting the hydrolysis of the more active chlorine liberated from a complex dichloramide (like the halazone in sample 1) and reacts only with the actual free chlorine present at any instance of time.[11, 12] The poor results from the analysis of sample 1 by this method do not, therefore, seem to be cause for rejection of the method but rather for its acceptance since it gave such excellent results in the analysis of samples 2 and 3 and appears to be more specific in the measurement of free chlorine than any of the others.

When the leuco crystal violet procedure for total chlorine was used, both the free and combined chlorine in sample 1 should have oxidized the iodide ion to hypoiodous acid, which in turn oxidizes the reagent to its highly colored form, crystal violet. The total chlorine content of sample 1 should, therefore, have been correctly determined by this method. As previously discussed, the one group that presumably did the test correctly did obtain good total-chlorine values (see Figure 3). A possible source of error in the total-chlorine procedure is the failure to dilute the sample to bring the total-chlorine concentration to less than 1 mg per liter as prescribed. If the total-chlorine concentration is greater than 1 mg per liter, the developed color has too great an absorbance for accurate measurement. This may be the explanation for some of the poor total-chlorine results.

Since the overall results of this study indicate that the ferrous-DPD

method gave the best precision and accuracy, it is interesting to note that a British study[10] of 12 chlorine methods in 1965 concluded that, for the measurement of free chlorine in the presence of combined chlorine in water, the ferrous-DPD colorimetric method was the most satisfactory. Furthermore, since sample 1 contained both free and combined chlorine, and the combined chlorine is obtained by subtraction of the free chlorine from the total chlorine, this value probably provides the best evaluation of the methods; the subtraction tends to cancel certain systematic errors such as may occur in the weighing of the sample or in the use of an improperly prepared dilution water. If this premise is accepted, then again the ferrous-DPD procedure produced the best results - as is also true for sample 3, which contained only combined chlorine.

The poor results obtained in this study by the use of the orthotolidine, and orthotolidine-arsenite methods may be due in part to the use of old permanent glass color comparators or of old permanent liquid-type standards prepared from chromate-dichromate solutions. Both tend to deteriorate slightly with age or may be off on preparation and should occasionally be checked by comparison with temporary standards prepared from chlorine. This does not, however, explain the poor results obtained with the ferrous-OT method, since all results for this method were obtained by titration.

COMMENTS OF THE PARTICIPANTS

METHYL ORANGE

Several participants mentioned that although the reagents were stable, the developed color was not and began to fade within 1 minute after sample addition; namely, the time of reaction was more critical than anticipated. Much variation in the solubility of the dry reagent methyl orange was also found. Another commented that it should be emphasized that acid, standard methyl orange, and sample should all be present at a pH of 2.0 ± 0.1. One participant stated that the manganese correction values were higher than the apparent concentration of available chlorine and hence were disregarded.

LEUCO CRYSTAL VIOLET

One participant reported that repeated analyses of free chlorine in sample 1 showed a consistently low result. It was also reported that the curve for free chlorine was linear only to 0.8 mg/liter, and this observation seemed to agree with that of another participant, who stated that the range of 0.1 to 1.0 mg/liter for total chlorine was much too concentrated to be read on a Beckman B spectrophotometer. Another participant found free-chlorine results varied as much as 12 percent when triplicate samples were run and total chlorine as much as 25 percent when six samples were run.

FERROUS-DPD TITRATION

One participant commented that the sharp endpoints were a big advantage over the iodometric titration. Another, however, observed a fading endpoint. It was also reported that both free- and total-chlorine results checked within 1 or 2 percent when triplicate samples were run. One analyst observed backdrift of red color in all samples, including blanks with and without addition of potassium iodide.

SNORT

Numerous comments were made about the developed color's fading too rapidly. One analyst found that total-chlorine results were always less than the sum of free chlorine plus monochloramine, even after volume correction. It was also stated that this method shows a deviation from Beer's Law. Another commented that the results were found to be reproducible.

IODOMETRIC TITRATION

The four participants commenting on this method agreed that the endpoint was difficult to detect at such small concentrations. Considerable driftback of color was also noted.

ORTHOTOLIDINE (OT)

One participant noted no difference in free-chlorine results run at 20°C and 1°C, nor in total chlorine by adding reagent before or after sample. Lower total chlorine results were, however, obtained when samples were cooled to 1°C. Several participants noted that the color development upon the addition of orthotolidine was much slower than stated in the literature and was extremely unstable. One stated that sample 1 took about 31 minutes to reach maximum color for total chlorine. Another reported that color was still increasing after 30 minutes with sample 1. A third commented that the total chlorine reported for sample 1 was read at 4 to 5 minutes. After 35 minutes, however, the value increased from 1.34 to 1.78 mg/liter. On the other hand sample 3 reached maximum absorbance in 4 minutes for total chlorine. The comment was also made that this test showed greater reproducibility than the methyl orange test. Another found that the standards were questionable since, when iodometrically standardized hypochlorite solutions were diluted with chlorine-free, chlorine-demand-free water, they were found to be subject to rapid change.

ORTHOTOLIDINE-ARSENITE (OTA)

One participant felt that the precision of this test was poor. Several

participants found that it takes too long to add sample and arsenite to the reagent to get the lowest possible free-chlorine result. Another stated that after the determination, a further color development was observed and a maximum absorbance was recorded after 40 minutes. A fourth stated that it was impossible to get a result on sample 3, since it had already started to turn before it could be got into the comparator, and sample 2 cooled to 1°C showed much less free chlorine (0.5 mg/liter) than before being cooled (0.8 mg/liter), probably because of time delay. As a result it was suggested that the need for rapid addition of the sample and reagents should be stressed. One commented that a graduated cylinder is convenient for dispensing the sample and that a dropping pipet calibrated to deliver the proper volume will allow rapid dispensing of the reagent.

AMPEROMETRIC TITRATION

Several found that if the instrument is used to determine free chlorine after making a test for total chlorine, some of the residual iodide will cause chloramines to titrate as free chlorine. This effect may be overcome by making a free-chlorine titration of distilled water to the endpoint before employing the instrument for actual sample processing.

FERROUS-ORTHOTOLIDINE TITRATION (FERROUS-OT)

One participant commented that Skoog and West (Fundamentals of Analytical Chemistry, Holt, Rinehart and Winston, 1963: p. 496) and others have reported the unsuitability of Mohr's salt as a primary standard because of variation from the theoretical composition. The Fe (II) titer of two ferrous ammonium sulfate solutions, prepared separately, was found to be approximately 10 percent below theoretical. Accordingly, the Fe (II) solution should be standardized before analysis is undertaken. Several participants had trouble with reproducibility on duplicate samples and encountered dubious endpoints. On the other hand, one analyst commented on the sharp endpoints and reproducible results and suggested that, in determining chloramines, addition of titrant while the color mixture is acidic may result in overtitration if the brown color is not due to dichloramine color but to the charring effect of acid. There was also some confusion about the calculation of total chlorine, and it was felt that there was such a small amount of chlorine to titrate and that there were so many reagents to be used and so many separate steps to be taken before each endpoint that accuracy was impossible, owing to the multiple sources of error.

SUMMARY AND CONCLUSIONS

Precision data developed by this study are useful only for comparison of methods and are not a true representation of the capability of a specific method, because of the variability in samples likely to be introduced by the method of preparation.

In general, the best overall accuracy and precision was shown by the ferrous-DPD[3] method, followed closely by the methyl orange,[1] SNORT,[4] and amperometric methods (see Table 5). The lack of accuracy of the old orthotolidine methods[6, 7, 9] make them the least acceptable, although all methods (with the possible exception of the ferrous-DPD) appear to have comparable precision. The statement in the SNORT procedure that chlorine-demand-free water is not necessary may have caused some difficulty with all of the methods since chlorine-demand-free water is mandatory for preparation of the samples. The generally low results for free chlorine suggest the likelihood of chlorine demand in the water, most likely in the form of ammonia.

The methyl orange[1] procedure produced good results, but several participants complained that the developed color was unstable. A possible source of difficulty in the methyl orange procedure might be the typographical error in section 4.2, line 13, that reads "-sample of the methyl orange-," and should read "-sample to the methyl orange-." It would be helpful also to add the information that 5 ml of methyl orange reagent will cover the range of 0 to 0.75 mg/liter, 10 ml for 0.5 to 1.9 mg/liter, and 15 ml for 1.25 to 2.75 mg/liter.

The leuco crystal violet[2] procedure produced poor results for sample 1 but was quite acceptable for samples 2 and 3 (see Table 5). This method is evidently more specific for actual free chlorine and inhibits the hydrolysis of chlorine in materials such as halazone.

The iodometric[5] procedure produced only mediocre results and is obviously not suitable for such small concentrations of total chlorine.

Despite the varied potential sources of error in the methods studied, the greatest source of error in chlorine measurement is probably in the use of distilled water that is not completely free of chlorine or of chlorine demand.

Table 5. SUMMARY OF OVERALL PRECISION AND ACCURACY

Method	Sample 1 Free	Sample 1 Combined	Sample 1 Total	Sample 2 Free	Sample 2 Total	Sample 3 Combined	Sample 3 Total	Average
				Average Mean Error				
Ferrous-DPD	0.120	0.063	0.079	0.158	0.115	0.013	0.052	0.086
Methyl Orange	0.183	0.007	0.132	0.176	0.047	0.028	0.091	0.095
SNORT	0.069	0.139	0.227	0.102	0.119	0.011	0.013	0.097
Amperometric	0.249	0.112	0.161	0.200	0.079	0.106	0.055	0.137
Leuco Crystal Violet	0.499	0.159	0.339	0.057	0.024	0.034	0.006	0.160[a]
Ferrous-OT	0.314	0.176	0.471	0.332	0.238	0.141	0.164	0.262
Orthotolidine	0.305	0.581	0.757	0.340	0.215	0.150	0.129	0.354
Orthotolidine-As	0.330	0.625	0.907	0.339	0.186	0.155	0.091	0.376
Iodometric	-----	-----	0.306	-----	0.198	-----	0.118	0.027
				Average Standard Deviation				
Ferrous-DPD	0.145	0.077	0.164	0.255	0.222	0.120	0.113	0.156
Amperometric	0.237	0.161	0.209	0.254	0.174	0.214	0.145	0.199
Orthotolidine-As	0.323	0.168	0.323	0.242	0.147	0.198	0.154	0.222
Ferrous-OT	0.282	0.258	0.357	0.247	0.202	0.120	0.123	0.227
Orthotolidine	0.341	0.160	0.343	0.297	0.212	0.174	0.190	0.246
Methyl Orange	0.341	0.163	0.338	0.268	0.188	0.224	0.220	0.249
SNORT	0.207	0.186	0.419	0.243	0.197	0.266	0.238	0.251
Leuco Crystal Violet	0.372	0.572	0.483	0.243	0.204	0.172	0.222	0.324[b]
Iodometric	-----	-----	0.360	-----	0.174	-----	0.169	0.234

[a] 0.030 with results on sample 1 excluded.

[b] 0.210 with results on sample 1 excluded.

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2. 4, 4', 4"-Methylidynetris (N, N-dimethylaniline) Method for Residual Chlorine (Leuco Crystal Violet). Appendix B.

3. Ferrous Method for Free Available Chlorine, Monochloramine Dichloramine, and Nitrogen T ichloride (Ferrous-DPD). Appendix C.

4. Stabilized Neutral Orthotolidine (SNORT) Method for Residual Chlorine and Iodine. Appendix D.

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APPENDICES

APPENDIX A.

METHYL ORANGE METHOD FOR DETERMINATION OF RESIDUAL CHLORINE

1. GENERAL DISCUSSION

1.1. Principle: Free chlorine bleaches a methyl orange solution quantitatively. In the pH range below 3, methyl orange has a red color with an absorption spectrum that exhibits a maximum at a wavelength of 510 mμ. By measuring the change in absorption at 510 mμ, the concentration of free chlorine in a sample containing a known amount of methyl orange may be established. At pH 2 or more the rate of reaction of chloramines with methyl orange is very slow. In the presence of excess bromide ion, chloramines also bleach methyl orange rapidly. Sodium bromide may, therefore, be added to the sample after the free-chlorine concentration has been determined, and the additional decrease in absorption will be due to chloramines.

It is important that there be an excess of methyl orange reagent at all times. If methyl orange is added to the sample, or if the sample is added with insufficient mixing, the chlorine present will not bleach the methyl orange quantitatively. The sample must therefore be added to the reagent with rapid mixing. When the addition of the sample to methyl orange produces a colorless solution, the need for a larger quantity of methyl orange is indicated. The additional methyl orange should not be added to the mixture, but instead the test should be repeated with a new sample and the larger quantity of methyl orange.

1.2. pH Control: The final pH of the sample reagent should be approximately 2. A higher pH results in incomplete color development, and a lower pH increases interference by chlorine-ammonia compounds. Either hydrochloric or chloroacetic acid may be used to adjust the pH. For samples with a limited range of alkalinity, hydrochloric acid is a more convenient reagent. Three drops of 6N HCl suffice for a total alkalinity up to 300 mg/liter as $CaCO_3$ and four drops for a total alkalinity of 300 to 600 mg/liter. The use of 1 ml of chloroacetic acid solution provides the optimum pH in samples containing up to 1,000 mg/liter alkalinity in a 50-ml sample.

1.3. Interference: Although suspended matter interferes, if the amount of suspended matter is low, a "blank reading" of sample without methyl orange may be used to correct the absorbance. Chloride ion interferes, but the addition of 1 mg/ml chloride ion to the methyl orange reagent eliminates the interference of chloride in concentrations to 1,000 mg/liter. In the presence of bromide, chlorine-ammonia compounds

will interfere, the extent of interference depending upon the bromide concentration. Bromine and bromine-ammonia compounds also interfere, producing a false chlorine reading equivalent to the active concentration of the bromine compound present. Ferric and nitrite ion in concentrations up to 10 mg/liter do not interfere. Manganic ion (0 to 3 mg/liter) bleaches methyl orange quantitatively, but the bleaching due to manganese may be evaluated by treating a sample with sodium arsenite at pH 7 before testing. Sodium arsenite selectively reduces residual chlorine so that the decrease in absorbance in the subsequent test may be assumed to be due to the equivalent manganic ion.

2. APPARATUS

Colorimetric equipment: One of the following is required.

2.1. Spectrophotometer, for use at 510 mμ and providing a light path of 1 cm.

2.2. Filter photometer, providing a light path of 1 cm and equipped with a green color filter exhibiting a maximum transmittance near 510 mμ.

3. REAGENTS

Prepare all reagents with ammonia-free distilled water.

3.1. Stock methyl orange solution: Dissolve 500.0 mg $C_{14}H_{14}N_3SO_3Na$ and dilute to 1,000 ml.

3.2. Standard methyl orange solution: Dilute 100 ml stock methyl orange solution to 1,000 ml after adding 1.67 g sodium chloride, NaCl. The reagent is stable indefinitely.

3.3. Acid solution: Either chloroacetic or hydrochloric acid may be used.

a. Chloroacetic acid solution: Dissolve 91 g $CH_2ClCOOH$ and dilute to 100 ml.

b. Hydrochloric acid, 6N. 1 + 1.

3.4. Arsenite buffer: Grind a mixture of 125 mg sodium arsenite, $NaAsO_2$; 375 mg citric acid, $C_6H_8O_7$; 14.5 g sodium citrate dihydrate, $Na_3C_6H_5O_7 \cdot 2H_2O$, together as a dry powder. This buffer produces a final pH of 7 when 100 mg is dissolved in the sample.

3.5. Sodium bromide solution: Dissolve 2.5 g NaBr in 100 ml.

4. PROCEDURE

The following procedure is suitable for chlorine concentrations to 2 mg/liter. Where the total available chlorine concentration exceeds 2 mg/liter, dilute the sample with double-distilled, ammonia-free water, or extend the standard calibration curve for methyl orange by the use of larger aliquots of methyl orange.

4.1. Calibration curves: Prepare the standard calibration curves by diluting an iodometrically standardized stock solution of chlorine or hypochlorite and following the procedure given in Sec. 4.2. Plot the absorbance versus free chlorine concentration. For greatest accuracy, perform the calibration at a temperature near that of the samples to be tested, because the absorbance of methyl orange solutions is slightly dependent upon temperature. For routine measurements in the 10 to 30°C range, the error from this source is negligible.

4.2. Free available chlorine: To determine free chlorine, combine 5.0 ml standard methyl orange solution and the proper volume of acid solution for pH adjustment. Use 1 ml chloroacetic acid solution or 3 to 4 drops (0.15 to 0.20 ml) 6N HCl. The final pH must be 2.0 ± 0.1. Add the 50-ml sample with mixing. After 1 to 1.5 min, measure the absorbance at 510 mμ, using a 1-cm light path. If the absorbance is greater than 0.10, determine the apparent concentration of free chlorine from the standard calibration curve. If the absorbance is less than 0.10, repeat the test, using 10 ml standard methyl orange solution, or dilute the sample with chlorine-demand-free water.

If manganese is present, first dissolve 100 mg arsenite buffer reagent in the 50-ml sample to reduce the free chlorine present. Then add the sample of the methyl orange-chloroacetic or hydrochloric acid mixture and measure the absorbance at 510 mμ after 2 to 2.5 min. Subtract the apparent free chlorine due to manganese from the free chlorine ascertained by the preceding determination.

4.3. Total available chlorine: To determine total chlorine, add 0.5 ml sodium bromide solution to the sample-reagent mixture after the determination of the free chlorine. Allow 10 min for the reaction of the chlorine-ammonia compounds and again measure the absorbance. If manganese is present, apply the above-mentioned correction to both the free- and total-chlorine results.

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APPENDIX B.

4, 4', 4"-METHYLIDYNETRIS (N, N-DIMETHYLANILINE) METHOD FOR RESIDUAL CHLORINE

1. GENERAL DISCUSSION

1.1. Principle: The compound 4, 4', 4"-methylidynetris (N, N-dimethylaniline), also known by the trivial name of leuco crystal violet, reacts instantaneously with free chlorine to form a bluish color. Interference from combined available chlorine can be avoided by completing the test within a 5-minute interval. The correct color development in the free chlorine-leuco crystal violet reaction depends upon the following factors and conditions. (a) The solution must be buffered in the pH range of 3.6 to 4.3. (b) A mercuric chloride solution must be added to the sample either before the addition of a leuco crystal violet solution or more conveniently in the form of a mixed indicator. (c) The ratio by weight of leuco crystal violet to chlorine must be at least 30 to 1. (d) The free-chlorine concentration should not exceed 2.0 mg/liter. (e) The mixed indicator solution should be added to the sample in a standardized procedure as described in Sec. 4.1a. (f) The test should be completed within 5 minutes after the mixed indicator addition. (g) The sample temperature should not exceed 40°C.

The total-chlorine determination involves the reaction of the free and combined chlorine with iodide ion to produce hypoiodous acid, which in turn reacts instantaneously with leuco crystal violet to form the dye crystal violet. The color is stable for days and adheres to Beer's law over a wide range of total chlorine. The extreme sensitivity of the determination may necessitate the dilution of the sample with chlorine-demand-free water to bring the chlorine concentration to the desired range of 1.0 mg/liter total chlorine. The following factors are important in the total chlorine determination. (a) The solution must be at pH 3.6 to 4.3 during the reaction period. (b) There must be an initial contact of at least 15 seconds' duration between chlorine and iodide ion. (c) The initial iodide concentration must not exceed 40 mg/liter. (d) The total chlorine concentration should not exceed 1.0 mg/liter. Semipermanent color standards for the total-chlorine determination can be prepared from crystal violet for visual matching of samples and standards in nessler tubes or test tubes.

Leuco crystal violet is available commercially in a very pure form that readily dissolves in water acidified with perchloric acid. The concentration of perchloric acid must produce a pH of 1.5 or less in the final indicator reagent. The dissolution of leuco crystal violet with perchloric acid must be carried out in the darkness of amber glass, and the final solution stored in amber glass or opaque plastic containers to minimize reagent deterioration. Both leuco crystal violet and the developed crystal

violet dye are relatively inert, nontoxic substances, and no special precautions are required other than those normally observed in the handling of any chemical reagent.

The preparation and handling of the saturated mercuric chloride requires special precaution owing to the poisonous and corrosive nature of this chemical. The mixed indicator system, although containing a considerably diluted mercuric chloride solution, should likewise be handled with care.

Improved accuracy in the determination of residual chlorine with leuco crystal violet is possible through photometric measurements.

The importance of using only chlorine-demand-free water and scrupulously cleaned glassware is self-evident because the presence of ammonia in the dilution water or organic matter on the glassware can consume chlorine and result in low chlorine values.

1.2. Interference: No significant interference from combined available chlorine occurs when the free chlorine content is determined within 5 minutes after addition of indicator. Fifteen minutes after addition of indicator the apparent error in the free-chlorine determination is of the order of 0.04 mg/liter at 25°C in a sample containing 5.0 mg/liter combined residual chlorine.

The one interference deserving attention in the determination of free residual chlorine is manganic ion, which increases the apparent residual chlorine reading. When manganic ion is known to be present, the arsenite modification outlined in the OTA method in the 12th Edition of Standard Methods, page 101, can be applied, the leuco crystal violet indicator system being substituted for orthotolidine.

Nitrite, nitrate, and ferric compounds do not interfere, while the normal effect of organic compounds is to reduce the free available chlorine. If suspended matter or organic color is present, removal of or compensation for these substances may be accomplished as prescribed in the 12th Edition of Standard Methods, pages 99-100.

1.3. Minimum detectable concentration: 0.01 mg/liter free available chlorine, 0.005 mg/liter total available chlorine.

2. APPARATUS

2.1. Illumination: The light sources to be used for comparison of samples with standards are described in the 12th Edition of Standard Methods, Sec. 2.1, page 95.

2.2. Colorimetric equipment: One of the following is required.

a. Nessler tubes, matched, 50 ml, tall form.

b. Test tubes, matched, with a capacity of at least 10 ml of sample when the sample surface is near the top of the test tube.

c. Filter photometer, providing a light path of 1 cm or longer and equipped with an orange filter having maximum transmittance near 592 mμ.

d. Spectrophotometer, for use at 592 mμ, providing a light path of 1 cm or longer.

2.3. Cleaning of glassware: All glassware or plastic containers, including containers for storage of reagent solutions, must be entirely freed of organic matter. This objective can be attained by recourse to either the chlorination or chromic acid method after the glassware has been thoroughly cleaned with suitable detergent and rinsed with distilled water. The chromic acid method requires less total time, but care is necessary to protect the laboratory personnel from contact with the cleaning mixture.

a. Chlorination: Expose all glassware or plastic containers to water containing at least 10 mg/liter chlorine for 3 hr or more before use, and then rinse with chlorine-demand-free water. After rinsing, oven or air dry the glassware in an atmosphere free from organic fumes.

b. Chromic acid: Prepare the chromic acid solution by adding 1 liter concentrated sulfuric acid to 35 ml saturated sodium dichromate solution contained in a 2-liter beaker. Stir the mixture carefully until all of the sodium dichromate has dissolved. When cleaning glassware, carefully heat a suitable volume of chromic acid solution to approximately 50°C. (CAUTION: Use rubber gloves, safety goggles, and protective clothing in handling this cleaning agent.) Carefully pour the chromic acid solution into the glassware to be cleaned so that contact is made with the entire inside surface of the container. Allow the cleaning solution to remain in the glassware for 2 to 3 min or longer. Carefully empty the glassware of chromic acid solution and rinse thoroughly with chlorine-demand-free water. Oven or air dry the glassware away from organic or other chlorine-consuming fumes.

3. REAGENTS

3.1. Chlorine-demand-free water: Chlorine-demand-free water can be made by the chlorination or ion-exchange methods. In either case, best results are obtained when distilled water is used as the primary source.

a. Chlorination: Add sufficient chlorine to distilled water to destroy the ammonia. The amount of chlorine required will be about ten times the amount of ammonia nitrogen present; in no event should the initial residual be less than 1.0 mg/liter free chlorine. Allow the chlorinated water to stand overnight or longer; then expose to direct sunlight until all residual chlorine is discharged.

b. Ion exchange: Prepare a 3-foot column of approximately 2.5 to 5 cm diameter containing strongly acid cation and strongly base anion exchange resins. Several commercial mixed-bed resins, analytical grade (Amberlite MB-1), are available, but the analyst should satisfy himself that ammonia, chloramines, or other compounds that react with chlorine are removed. Pass the distilled water at a relatively slow rate through the resin bed and collect in a scrupulously cleaned receiver that will protect the treated water from undue exposure to the atmosphere.

c. Prepare all reagent solutions and dilute all samples with the chlorine-demand-free water.

3.2. Stock chlorine solution: Prepare the stock chlorine or hypochlorite solution from certain commercial solutions (Zonite, a product of Zonite Products Corp., contains approximately 1 per cent available chlorine; or household bleach), or by bubbling chlorine gas from a small lecture-size cylinder into distilled water. For convenience, adjust the chlorine concentration to approximately 100 μg per ml of solution. Standardize the stock solution by titrating a suitable aliquot with standard sodium thiosulfate titrant as described in the 12th Edition of Standard Methods, Iodometric Method A, Sec. 3.2 and 3.3, page 93, or by the amperometric titration method described on pages 103-108.

3.3. Chlorine solution for temporary total chlorine standards: If measurements of combined residual chlorine are desired, mix an ammonium sulfate solution with chlorine solution in an ammonia-to-chlorine ratio of at least 20 to 1. Dissolve 3.89 grams $(NH_4)_2SO_4$ in distilled water and dilute to 1,000 ml to form a solution containing 1.0 mg NH_3 per 1.0 ml. React each 2.0 ml $(NH_4)_2SO_4$ solution with each 1.0 ml stock chlorine solution, which contains 100 μg per 1.0 ml. Standardize the combined chlorine solution and use immediately for calibration purposes.

3.4. Buffer solution for free-chlorine determination, pH 4.0.

a. Potassium hydroxide, 4M. Dissolve 224.4 g KOH and dilute to 1 liter with chlorine-demand-free water.

b. Citric acid, 2M. Dissolve 384.3 g $C_6H_8O_7$, or 420.3 g $C_6H_8O_7 \cdot H_2O$, and dilute to 1 liter with chlorine-demand-free water.

c. Potassium citrate solution: To 350 ml 4M potassium hydroxide, add with stirring 700 ml 2M citric acid. If desired, prepare smaller volumes in the ratio of 1 volume of potassium hydroxide to 2 volumes of citric acid.

d. Acetate solution: Dissolve 161.2 g glacial acetic acid and 49.5 g sodium acetate, CH_3COONa, or 82.1 g $CH_3COONa \cdot 3H_2O$, and dilute to 1 liter with chlorine-demand-free water.

e. Final buffer solution: Mix equal volumes of potassium citrate solution (c) with acetate solution (d) to make the final pH 4.0 buffer solution for the free-chlorine determination.

3.5. Stock leuco crystal violet reagent: Measure 500 ml chlorine-demand-free water and 14.0 ml 85 percent ortho-phosphoric acid into a brown glass container of at least 1-liter capacity. Introduce a magnetic stirring bar into the container and mix the acidified water at moderate speed. Add 3.0 g 4,4',4''-methylidynetris(N,N-dimethylaniline), Eastman Chemical No. 3651, and continue agitation until dissolution is complete. Finally, add 500 ml chlorine-demand-free water. Store in the brown bottle at room temperature away from direct sunlight. Discard after 6 months. If a rubber stopper must be used, wrap with Saran or other plastic wrapping material to protect from contact with the reagent.

3.6. Saturated mercuric chloride solution: To 20 g $HgCl_2$ contained in a 300-ml flask, add 200 ml chlorine-demand-free water. Gently agitate for a few minutes and let stand for 24 hr. (CAUTION: Label the container with the warning that mercuric chloride is poisonous and corrosive.)

3.7. Mixed indicator: To 600 ml stock leuco crystal violet reagent in a brown bottle, add 50 ml saturated mercuric chloride solution and swirl to ensure complete mixing. If desired, prepare smaller volumes of mixed indicator in the ratio of 12 volumes stock leuco crystal violet reagent to 1 volume saturated mercuric chloride solution. Follow the storage directions prescribed in Sec. 3.5 for the stock leuco crystal violet reagent.

3.8. Buffer solution for total chlorine determination, pH 4.0. Dissolve 480 g glacial acetic acid and 148 g sodium acetate, CH_3COONa, or 243 g $CH_3COONa \cdot 3H_2O$, in 400 ml chlorine-demand-free water and dilute to 1 liter. Transfer the solution to a brown bottle. Add 3.0 g potassium iodide, KI, to the bottle and shake the bottle to dissolve the salt. Store the solution in the brown bottle and avoid undue exposure to the air.

3.9. Solutions for preparation of semipermanent total-chlorine standards:

a. Buffer solution, pH 4.0. Dissolve 480 g glacial acetic acid and 146 g sodium acetate, CH_3COONa, or 243 g $CH_3COONa \cdot 3H_2O$, in 400 ml chlorine-demand-free water and dilute to 1 liter.

b. Crystal violet solution: Dissolve 40.0 mg crystal violet, Eastman Chemical No. C 1350, in 500 ml chlorine-demand-free water containing 20 ml pH 4.0 buffer solution (3.9a). Stir for 30 min or more to effect complete dissolution, then dilute to 1,000 ml with chlorine-demand-free water.

4. PROCEDURE

4.1. Temporary chlorine standards: Temporary standards are recommended for photometric calibration and research work as well as for visual comparison. Two separate sets of temporary chlorine standards are mandatory because of the divergent colors developed by free and combined residual chlorine. Semipermanent color standards for the total-chlorine determination can be prepared from crystal violet dye and have a longevity approaching 3 months. The color system produced with free residual chlorine, on the other hand, differs from the normal crystal violet shade and is stable for only a few days. Commercially prepared standards may be purchased from the La Motte Chemical Products Co., Chestertown, Maryland 21630, at this time, but it is hoped that a method of preparing standards will be available to all in the near future.

a. Preparation of temporary free-chlorine standards: Thoroughly clean all glassware as described in Sec. 2.3 and preferably air or oven dry before use. Prepare temporary chlorine standards from a suitable volume of stock chlorine solution added to 2 liters of chlorine-demand-free water contained in an amber glass bottle. Set up a chlorine series in the range of 0.1 to 2.0 mg/liter at increments of 0.1 or 0.2 mg/liter for visual comparison studies. Standardize the dilute chlorine solutions by means of the sodium thiosulfate or amperometric titration methods.

After standardization, measure exactly 50 ml dilute chlorine solution into a 100-ml glass-stoppered volumetric flask, taking care to introduce the chlorine solution with a minimum of agitation into the volumetric flask. By means of a Mohr pipet, add 1.0 ml pH 4.0 buffer solution, Sec. 3.4, and gently swirl the flask to mix. With another measuring pipet, add 1.0 ml mixed indicator, Sec. 3.7. Standardize the mixed indicator addition in the following manner. After filling the measuring pipet to the mark, position the pipet tip inside the neck of the volumetric flask so that the tip makes contact with the inside glass surface, and allow the mixed indicator to flow down the inside glass surface to the sample with a minimum of initial agitation of the sample. Remove the pipet from the flask and swirl the contents with a quick firm motion to

effect intimate contact between the mixed indicator and the sample. These steps produce the highest and most consistent absorbance values.

Transfer the colored temporary standards to 50-ml nessler tubes for visual comparison, or prepare a photometric calibration curve.

Visual comparison: If the temporary standards are prepared directly in 50-ml nessler tubes, stopper the tube after addition of the mixed indicator, and mix quickly by inverting the tube several times. If a smaller sample volume is taken, as, for example, 10 ml contained in a test tube, reduce the quantity of pH 4.0 buffer and mixed indicator to 0.2 ml each.

Photometric calibration: Transfer the colored temporary standards of known free-chlorine concentration to cells of 1 cm light path or longer, and read the absorbance in a photometer at a wavelength of 592 mμ against a distilled water reference. Plot the absorbance values versus chlorine concentrations to construct a curve that approximates Beer's law in the lower free-chlorine range and exhibits a slight curvature with the higher free-chlorine concentrations.

b. Preparation of temporary total-chlorine standards: Prepare standardized solutions in the total-chlorine range of 0.1 to 1.0 mg/liter. Pipet a 50-ml sample into a 100-ml volumetric flask or 50-ml nessler tube. Add 0.5 ml total-chlorine buffer, Sec. 3.8, mix, and allow a contact period of at least 15 sec. Add 0.5 ml mixed indicator and mix to develop the color. No special precautions are necessary in the addition and mixing of these solutions.

Photometric calibration: Construct a calibration curve by measuring the absorbance values of the temporary total-chlorine standards at 592 mμ, preferably in 1-cm cells.

4.2. Semipermanent total-chlorine standards: The variable composition of commercially available crystal violet dye necessitates a reconcilement of the absorbance of the semipermanent standards with the photometric calibration curve. The final semipermanent standards should be adjusted into agreement with the calibration absorbance values obtained on temporary total-chlorine standards.

Add the specified volume of crystal violet solution to a 200-ml volumetric flask containing 100 ml distilled water and 4.0 ml pH 4.0 buffer solution, Sec. 3.9a. Dilute to volume with distilled water and compare the absorbance at 592 mμ with the suggested values given in Table B-1 or with the photometric calibration curve. Protect the standards from direct sunlight and exposure to air to maintain stability for approximately 3 months. Seal the standards in glass ampoules for maximum protection.

Table B-1. SEMIPERMANENT TOTAL-CHLORINE STANDARDS

Total-chlorine standard, mg/liter	Crystal violet solution, ml	Absorbance of final 200-ml standard at 592 mμ in 1-cm cell
0.1	2.84	0.131
0.2	5.80	0.268
0.3	8.60	0.396
0.4	11.60	0.530
0.5	14.40	0.660
0.6	17.30	0.790
0.7	20.00	0.925
0.8	23.20	1.060
0.9	26.60	1.192
1.0	28.80	1.320

4.3. Color development of free-chlorine sample: To ensure the highest accuracy and reproducibility of results, apply the mixed indicator to the unknown sample in the same uniform manner prescribed for the temporary standards in Sec. 4.1a. Match the test sample visually with the temporary standards, or read the absorbance photometrically and refer to the standard calibration curve for the free-chlorine equivalent. Complete the determination within 5 min of the addition of the mixed indicator to obviate interference from combined residual chlorine composed of mono-, di-, and tri-chloramine and manifested by a slow increase in color.

The color development due to combined chlorine residuals is negligible at sample temperatures as high as 40°C and slightly accelerated at higher temperatures. The color with free chlorine develops instantaneously, and in the absence of combined residual chlorine is stable for several days.

4.4. Color development of total-chlorine samples:

a. Concentrations less than 1.0 mg/liter. Measure a 50-ml sample into a suitable flask or tube and add 0.5 ml total-chlorine buffer, Sec. 3.8. Mix and wait at least 60 sec. Add 1.0 ml mixed indicator, mix, and visually match with standards or read the absorbance photometrically and compare with the calibration curve.

b. Concentrations more than 1.0 mg/liter: Place approximately 25 ml chlorine-demand-free water in a flask or tube calibrated to contain at least 50 ml. Add 0.5 ml total-chlorine buffer, Sec. 3.8, followed by a known volume of 25 ml or less of the unknown sample. After mixing, let stand for at least 60 sec. Add 1.0 ml mixed indicator, mix, and dilute to the mark with chlorine-demand-free water. Match visually with standards or read the absorbance photometrically and compare with the calibration curve. Select one of the following sample volumes in order to remain within the optimum chlorine range:

Total chlorine, mg/liter	Sample volume required, ml
1.0 to 2.0	25
2.0 to 2.5	20
2.5 to 3.0	15
3.0 to 5.0	10
5.0 to 10.0	5

The total-chlorine color develops instantaneously and remains stable for days. The final color, if too intense for visual matching, may be diluted, matched with standards, and the initial total chlorine estimated by applying the dilution factor.

4.5. Compensation for turbidity and color: Compensate for the presence of natural color turbidity as described in Standard Methods, Sec. 7.4, pages 99 and 100.

5. CALCULATION

$$\text{mg/liter total Cl} = \frac{A \times 50}{\text{ml sample}}$$

$$\text{mg/ liter combined Cl} = B - C$$

where A = total chlorine measured in mg/liter, B = total chlorine in mg/liter, and C = free chlorine in mg/liter.

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APPENDIX C.

FERROUS METHOD FOR FREE AVAILABLE CHLORINE, MONOCHLORAMINE, DICHLORAMINE, AND NITROGEN TRICHLORIDE

1. GENERAL DISCUSSION

1.1. Principle: N, N-diethyl-p-phenylenediamine (DPD) has been introduced by Palin[1] for use in the ferrous method in place of neutral orthotolidine. The colors produced are more stable, fewer reagents are required, and a full response in neutral solution is obtained from dichloramine. In the titrimetric procedure, decolorization by standard ferrous ammonium sulfate (FAS) titrant is instantaneous and thereby permits each step to be performed more rapidly. In the colorimetric version of the method, the standard colors are prepared by use of a standard potassium permanganate solution. Where complete differentiation is not required, the procedure may be further simplified to give only free and combined available chlorine or total residual available chlorine.

In the absence of iodide ion free available chlorine reacts instantly with the N, N-diethyl-p-phenylenediamine (DPD) indicator to produce a red color. Subsequent addition of a small amount of iodide ion acts catalytically to cause monochloramine to produce color. Further addition of iodide ion to excess evokes a rapid response from dichloramine. Unlike the reaction with neutral orthotolidine, any nitrogen trichloride present no longer displays color with free available chlorine but is included with dichloramine. By adding iodide ion before DPD, however, a proportion of the nitrogen trichloride is caused to appear with free available chlorine. A supplementary procedure based upon altering in this way the order of adding the reagents thus permits the estimation of nitrogen trichloride.

Chlorine dioxide appears, to the extent of one-fifth of its total available chlorine content, with free available chlorine. A full response from chlorine dioxide, corresponding to its total available chlorine content, may be obtained if the sample is first acidified in the presence of iodide ion and subsequently brought back to an approximately neutral pH by addition of bicarbonate ion. Bromine, bromamine, and iodine react with DPD indicator and appear with free available chlorine, DPD procedures for the determination of these halogens and related compounds have been developed.[2, 3]

In a recent comparison of methods for the determination of both free chlorine and chloramines in water it was concluded that the best colorimetric method was the DPD method and the best all-round method the DPD-FAS titration.[4, 5]

1.2. pH Control: For accurate results careful pH control is essen-

tial. At the proper pH of 6.2 to 6.5, the red colors produced may be titrated to sharp colorless endpoints. The titration must be carried out as soon as the red color is formed in each step. Too low a pH in the first step will tend to make the monochloramine show in the free-chlorine step and the dichloramine in the monochloramine step. Too high a pH may cause dissolved oxygen to give a color.

1.3. Temperature control: In all methods for differentiating free chlorine from chloramines the higher the temperature the greater the tendency for the chloramines to react with the reagents and thus lead to increased apparent free-chlorine results after a fixed time interval. The exceptions to this are the titration methods, probably due to the speed with which the titration is completed compared with the 2 to 3 minutes required for the colorimetric measurement to be made. The DPD methods are among those least affected by temperature.[5]

1.4. Interference: The only interfering substance likely to be encountered in water is oxidized manganese. To correct for this, place 5 ml of buffer solution, one small crystal of potassium iodide, and 0.5 ml of sodium arsenite solution (500 mg $NaAsO_2$ plus 100 ml distilled water) in the titration flask. Add 100 ml of sample and mix. Then add 5 ml of DPD indicator solution, mix, and titrate with standard ferrous ammonium sulfate titrant until any red color is discharged, or measure colorimetrically. The reading is subtracted from reading A obtained by the normal procedure as described in Sec. 3.1a of this method. If the combined reagent in powder form (see below) is used, the potassium iodide and arsenite are first added to the sample and mixed, the combined buffer-indicator reagent being added afterwards.

Interference by copper up to approximately 10 mg/liter copper is overcome by the EDTA incorporated in the reagents. The presence of EDTA also enhances the stability of the DPD indicator solution by retarding deterioration due to oxidation and in the test itself provides virtually complete suppression of dissolved oxygen errors by prevention of trace metal catalysis.

2. REAGENTS

2.1. Phosphate buffer solution: Dissolve 24 g anhydrous disodium hydrogen phosphate, Na_2HPO_4, and 46 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, in distilled water. Combine this solution with 100 ml distilled water in which 800 mg disodium ethylenediamine tetraacetate dihydrate, also called (ethylenedinitrilo) tetraacetic acid sodium salt, have been dissolved. Dilute to 1 liter with distilled water and add 20 mg mercuric chloride to prevent mold growth.

2.2. N, N-diethyl-p-phenylenediamine (DPD) indicator solution: Dissolve 1 g DPD Oxalate (Eastman Chemical No. 7102) or 1.5 g

p-amino-N:N-diethylaniline sulphate (British Drug Houses chemical available from Gallard-Schlesinger Chemical Mfg. Corp., 584 Mineola Ave., Carle Place, Long Island, N. Y., 11514) in chlorine-free distilled water containing 8 ml 1 + 3 sulfuric acid and 200 mg disodium ethylenediamine tetraacetate dihydrate. Make up to 1 liter, store in an amber glass-stoppered bottle, and discard when discolored. (The buffer and indicator are commercially available as a combined reagent in stable powder form.)

2.3. Standard ferrous ammonium sulfate (FAS) titrant: Dissolve 1.106 g Mohr's salt, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water containing 1 ml of 1 + 3 sulfuric acid and make up to 1 liter with freshly boiled and cooled distilled water. This is a primary standard and may be used for 1 month. Potassium dichromate may be used to check the titer. The FAS titrant is equivalent to 100 μg Cl per 1.00 ml.

2.4. Potassium iodide crystals.

2.5. Potassium iodide solution: Dissolve 50 g KI and dilute to 1 liter, using freshly boiled and cooled distilled water. Store in a brown, glass-stoppered bottle, preferably in a refrigerator. Discard the solution when a yellow color develops.

3. PROCEDURE

The quantities given below are suitable for concentrations of total available chlorine up to 4 mg/liter. Where the total chlorine exceeds 4 mg/liter, use a smaller sample and dilute to a total volume of 100 ml. Mix the usual volumes of buffer reagent and DPD indicator solution, or the usual amount of DPD powder, with distilled water before adding sufficient sample to bring the total volume to 100 ml.

3.1. Free available chlorine or chloramine: Place 5 ml each of buffer reagent and DPD indicator solution in the titration flask and mix (or use about 500 mg of DPD powder). Add 100 ml sample and mix.

a. Free available chlorine: Titrate rapidly with standard FAS titrant until the red color is discharged (reading A).

b. Monochloramine: Add one very small crystal of potassium iodide and mix; or if the dichloramine concentration is expected to be high, add 0.1 ml (two drops) potassium iodide solution and mix. Continue titration until the red color is again discharged (reading B).

c. Dichloramine: Add several crystals of potassium iodide (about 1 g) and mix to dissolve. Allow to stand for 2 minutes and then continue titration until the red color is again discharged (reading C).

In the case of very high dichloramine concentrations, allow a further 2 minutes standing if color driftback indicates slightly incomplete reaction. When dichloramine concentrations are not expected to be high, use half the specified amount of potassium iodide.

d. Simplified procedure for free and combined available chlorine or total available chlorine: Omit stage (b) so as to obtain monochloramine and dichloramine together as combined available chlorine. To obtain total available chlorine in one reading, add the full amount of potassium iodide at the start with the specified amounts of buffer reagent and DPD indicator, and titrate after 2 minutes' standing.

3.2. Nitrogen trichloride: The absence of color in the first step indicates the absence of nitrogen trichloride (and of chlorine dioxide). Nitrogen trichloride, readily identified by its distinctive odor, may be estimated by the following procedure. Place a small crystal of potassium iodide in a titration flask. Add 100 ml sample and mix. Then add the contents to a second flask containing 5 ml each of buffer reagent and DPD indicator solution (or about 500 mg DPD powder direct to the first flask). Titrate rapidly with standard FAS titrant until the red color is discharged (reading D).

Monochloramine is unlikely to be present with nitrogen trichloride. If high concentrations of dichloramine are present, use potassium iodide solution as in Sec. 3.1b, in place of a potassium iodide crystal.

3.3. Calibration of colorimeters: Instead of titrating with standard FAS titrant, a colorimetric procedure may be followed by using either the specified liquid reagents or the solid DPD powder in which the buffer and indicator are combined. To calibrate colorimeters, prepare a standard potassium permanganate solution containing 891 mg $KMnO_4$ per liter. Dilute 10 times for use, whereupon 1 ml made up to 100 ml with distilled water is equivalent to 1 mg/liter Cl. The standard colors produced after adding the prepared permanganate solutions to the buffer reagent and indicator, as in Sec. 3.1, may, after the calibration procedure, be titrated against standard FAS titrant solution as a check on the standard color and on any absorption of permanganate by the distilled water used.

4. CALCULATION

For a 100-ml sample, 1.00 ml standard FAS titrant equals 1.00 mg/liter available residual chlorine.

If monochloramine is present with nitrogen trichloride, which is unlikely, it will be included in reading D, in which case NCl_3 is obtained from 2(D-B).

Chlorine dioxide if present, is included in reading A to the extent of one-fifth of its total available chlorine content.

Reading	NCl_3 absent	NCl_3 present
A	free Cl	free Cl
B - A	NH_2Cl	NH_2Cl
C - B	$NHCl_2$	$NHCl_2$ + 1/2 NCl_3
D	--	free Cl + 1/2 NCl_3
2(D - A)	--	NCl_3
C - D	--	$NHCl_2$

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APPENDIX D.

STABILIZED NEUTRAL ORTHOTOLIDINE (SNORT) METHOD FOR RESIDUAL CHLORINE AND IODINE

1. GENERAL DISCUSSION

The orthotolidine method using hydrochloric acid (method B) measures both free and combined chlorine. Modifications of this method used to differentiate between free and combined chlorine, the flash test (method C), and the OTA test (method D), depend on the slightly slower rate of reaction of orthotolidine in acid solution with combined chlorine than with free chlorine. The rapid addition of reagents and temperatures near 1°C are required even with the flash test and OTA methods (C and D).

1.1. Principle: Orthotolidine is quite stable in the reduced form when stored in brown bottles in the presence of hydrochloric acid. The stability of oxidized orthotolidine decreases, however, as the pH increases. For this reason, orthotolidine has classically been used at pH 1.3 and lower. As the pH is increased, the rate of reaction of orthotolidine with nitrite, iron, and combined chlorine becomes slower and essentially disappears at pH 7. Although neutral orthotolidine was proposed[1] for an analytical method as early as 1939 and used by many others later,[2-6] the pH values used by these early workers were below 7, the pH required to minimize interference, because a stable product could not be produced at this pH. To obtain correct color development from free chlorine and orthotolidine, it is necessary to have the pH of the solution at 7.0 because of interferences at lower pH, and to produce stable colors at these high pH values it is necessary to add a stabilizer. It has been noted by Johnson[7,8] that anionic surface-active agents in general stabilize the orthotolidine product, and "Aerosol OT," a trademark of the American Cyanamid Co., sodium di(2-ethylhexyl) sulfosuccinate is the best stabilizing reagent found to date. The concentration of stabilizer required for best stability at high and low temperature is 40 mg for each 100 ml of sample plus reagents.

The ratio by weight of orthotolidine dihydrochloride to chlorine must be at least 8 to 1. With the concentration of orthotolidine recommended in the procedure the chlorine concentration must not exceed 6 mg/liter.

The pH of the final solution must be between 6.5 and 7.5 to minimize low pH interference and high pH fading. If the pH of the sample is less than 5 or greater than 9, and in addition the alkalinity is greater than 150 or the acidity greater than 200 mg/liter, the final pH of the solution should be checked. If the alkalinity is high and the final pH does not lie within the range 6.5 to 7.5, the sample should be adjusted to this range before analysis.

To ensure correct color development, minimum interference, a pH of 6.5 to 7.5, and a ratio of orthotolidine to free chlorine of at least 8 to 1, the sample must be added to the reagents.

The reaction time and temperature are relatively unimportant compared with the usual methods for chlorine determination. For extremely large ratios of combined chlorine to free chlorine, however, high temperature and long waiting times are undesirable. At 35°C a 1-mg/liter monochloramine solution produces a false free-chlorine residual of 0.01 mg/liter per minute. At high temperature and for long waiting times, color fading may become important, especially at less than 0.1 mg/liter free chlorine. A 1-mg/liter solution of free chlorine fades at the rate of 0.005 mg/liter per minute at 35°C.

Iodide can be added in neutral solution to measure monochloramine and in acidic solution to measure dichloramine. The reaction of iodide and chloramine yields a concentration of iodine equivalent to the chloramine. In the colorimetric procedure, orthotolidine is present with the chloramine when iodide is added, and the iodine produced by the chloramine is immediately reduced back to iodide and acts as a catalyst in generating an amount of blue orthotolidine equivalent to the original chloramine present. Because of this catalytic effect, lesser amounts of iodide are required compared with amperometric titration, which improves the separation of the monochloramine and dichloramine fractions.

Other comments in Standard Methods under the orthotolide method B, Sec. 1, General Discussion, are applicable regarding stability and preparation of orthotolidine, the use of chlorine-demand-free water, and precautions for the exclusion of laboratory fumes, reducing agents, and oxidizing agents from the reagents.

1.2. Interference: When orthotolidine or any other chromogenic reagent is used to measure residual chlorine, strong oxidizing agents of any kind form an interference. Such interferences include manganic compounds, chlorine dioxide, bromine, iodine, and ozone. The reduced form of these compounds, manganous ion, bromide, chloride, iodide, and oxygen do not, however, interfere with the method. Reducing agents such as ferrous compounds, hydrogen sulfide, and oxidizable organic matter do not form an interference in the analytical method but may interfere in maintaining chlorine residuals by reducing the chlorine residual by reaction with the chlorine to produce chloride ion, acting simply as chlorine demand.

Turbidity and color also interfere with the method as with any other colorimetric method unless the background turbidity or color are compensated for by using a blank. Concentrations of 55 mg/liter iron, 92 mg/liter nitrite, and 6,000 mg/liter chloride do not interfere. The inter-

ference of combined chlorine is insignificant in the determination of free chlorine except as noted before at high temperature and long waiting times. Manganic compounds produce up to stoichiometric interference but can be compensated for by using a blank. In the presence of greater than 0.01 mg/liter manganic manganese, a blank is prepared by adding 5 ml of sodium arsenite to a 100-ml sample. This sample is then added to the reagents as usual, and this blank is used as a reference in measuring the free chlorine present, either by zeroing the photometer with this blank or by using the blank as a reference when making color comparison.

If nitrogen trichloride is present, half reacts as free available chlorine, but the remainder does not interfere in the monochloramine and dichloramine measurements. Many different organic chloramines are possible. The extent to which these organic chloramines interfere in the monochloramine or dichloramine determination steps depends on the nature of the organic compound; they may appear in either or both fractions.

1.3. Minimum detectable concentration: The SNORT chlorine reaction is sensitive to free residual chlorine concentrations as small as approximately 0.01 mg/liter.

2. APPARATUS

Colorimetric equipment: One of the following is required.

2.1. Filter photometer, providing a light path of 1 cm or longer for 1 mg/liter free chlorine residual and less, or a light path from 1 to 10 mm above 1-1/2 mg/liter free chlorine residual; also equipped with a red filter having maximum transmission in the range of 600 to 650 mμ.

2.2. Spectrophotometer, for use at 625 mμ, providing a light path noted in Sec. 2.1.

3. REAGENTS

Chlorine-demand-free distilled water recommended below can be prepared as discussed in Chlorine-Orthotolidine Method B, Sec. 3.1. It is not an absolute requirement, because chlorine will generally react with the orthotolidine in the reagents before it can react with demand compounds.

3.1. Neutral orthotolidine reagent: Add 5 ml concentrated reagent-grade hydrochloric acid to 100 ml chlorine-demand-free distilled water. Add 5 ml of this acid solution and 1.5 g reagent-grade orthotolidine dihydrochloride to chlorine-demand-free distilled water and dilute to 1 liter. Store in a brown bottle and observe the other storage precautions in the

chlorine acid-orthotolidine method B. (CAUTION: Toxic; take care to avoid ingestion.)

3.2. Buffer-stabilizer reagent: Dissolve 25.9 g disodium hydrogen phosphate, Na_2HPO_4, 12.6 g potassium dihydrogen phosphate, KH_2PO_4, 8.0 g "Aerosol OT," di(2-ethylhexyl) sulfosuccinate, in a solution of 500 ml chlorine-demand-free water and 200 ml diethylene glycol monobutyl ether. Dilute to 1 liter with chlorine-demand-free water. The phosphates are reagent-grade chemicals. "Aerosol OT" can be obtained from the Fisher Scientific Co., Fairlawn, New Jersey, as their 100% solid reagent. Diethylene glycol monobutyl ether is also available from Fisher Scientific Co. as their "purified" reagent, boiling point 112 to 114°C at 13 mm of mercury.

3.3. Potassium iodide solution: Dissolve 0.4 reagent-grade KI in chlorine-demand-free distilled water and dilute to 100 ml. Store in a brown, glass-stoppered bottle, preferably in a refrigerator. Discard when a yellow color develops.

3.4. Sulfuric acid solution: Cautiously add 4 ml concentrated H_2SO_4 to chlorine-demand-free distilled water and dilute to 100 ml.

3.5. Sodium carbonate solution: Dissolve 5 g reagent grade Na_2CO_3 in chlorine-demand-free distilled water and dilute to 100 ml.

3.6. Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water and dilute to 1 liter. (CAUTION: Toxic; take care to avoid ingestion.)

4. PROCEDURE

4.1. Calibration of photometer: Construct a calibration curve by making dilutions of standardized hypochlorite solution prepared as directed under chlorine demand method A, Sec. 3.1. Observe the special precautions listed under chlorine-acid orthotolidine method B, Sec. 3.5. Use the same procedure as given below for the preparation of the calibration curve using standardized hypochlorite solutions as used for the sample.

4.2. Color development of free chlorine: Use 0.5 ml neutral orthotolidine and 0.5 ml stabilizer-buffer reagent with 10-ml samples and 5 ml neutral orthotolidine and 5 ml stabilizer-buffer reagent with 100 ml, and the same ratio for other volumes. Place the neutral orthotolidine and stabilizer-buffer mixture in the photometer tube or a 250-ml beaker on a magnetic stirrer. Mix the reagent slightly and add the sample to the reagents with gentle stirring. Measure the percent transmittance and convert to absorbance at 625 mμ. The value obtained (A) from the

calibration curve represents the free-chlorine residual. To minimize possible interferences from large concentrations of combined chlorine and high temperature fading, the normal time used between mixing of the sample with the reagents and reading on the photometer is approximately 2 minutes.

4.3. Monochloramine: Return any aliquot used for measuring free chlorine, Sec. 4.2., to the sample. Add with stirring 0.5 ml potassium iodide solution to each 100-ml sample or a similar ratio for other sample volumes. The value obtained (B) from the calibration curve represents the free-chlorine plus monochloramine residuals.

4.4. Dichloramine: Return any aliquot used for measuring the monochloramine, Sec. 4.3., to the sample. Add with stirring 1 ml sulfuric acid solution to each 100-ml sample or a similar ratio for other sample volumes. Allow 30 seconds for color development. Add 2 ml sodium carbonate solution slowly with stirring or until a pure blue solution returns. The value obtained (C) represents, with a slight dilution correction, the total chlorine residual: free chlorine, monochloramine, and dichloramine.

4.5. Compensation of interferences: Compensate for the presence of natural color or turbidity as well as manganic compounds by adding 5 ml arsenite to 100 ml sample. Add this blank sample to the reagents as above. Use the color of the blank to set 100% transmittance or zero absorbance on the photometer. Measure all samples relative to this blank. Read from the calibration curve the concentrations of free chlorine present in the sample.

5. CALCULATION

mg/liter free chlorine residual = A (including one half of trichloramine if present)

mg/liter monochloramine = B - A (as mg/liter Cl)

mg/liter dichloramine = 1.03 C - B (as mg/liter Cl)

mg/liter total chlorine = 1.03 C (as mg/liter Cl)

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APPENDIX E.

TABULATION OF RESULTS

Table E-1. Sample 1, Free Chlorine (0.83 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.07	2	1136	0.90	7
1	0.86	3	1136	0.78	3
1	0.85	4	1314	0.85	8
2	0.78	4	1314	0.82	6
2	0.16	2	1611	0.70	7
2	0.76	8	1611	0.65	9
3	0.72	1	2112	0.21	2
3	0.79	7	2112	1.05	1
3	0.82	3	2222	0.15	3
3	0.80	8	2222	0.10	6
5	1.50	8	2222	0.12	8
6	0.54	8	2223	0.30	7
7	0.70	8	2223	0.28	1
7	0.00	2	2311	0.93	1
8	0.38	2	2311	0.90	3
8	0.64	8	2311	0.92	4
9	0.80	6	2411	0.78	4
10	0.02	2	2411	0.78	1
10	0.02	3	2411	0.06	2
11	0.53	1	2411	0.76	8
1114	0.16	2	2926	1.04	1
1114	0.64	3	2926	1.15	9
1114	0.38	8	3122	0.37	8
1136	0.80	6	3122	0.70	3

(Table E-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3122	0.60	7	3811	0.50	2
3221	0.40	9	4212	0.75	7
3221	0.30	6	4212	0.85	6
3221	0.40	3	4212	0.72	3
3222	1.15	4	4421	0.54	1
3222	1.35	8	4421	0.32	9
3222	1.30	2	4511	0.90	3
3226	0.07	1	4511	0.45	9
3314	0.17	7	4516	0.76	6
3314	0.15	2	4516	1.10	4
3314	0.16	4	4516	0.17	2
3416	0.41	9	4611	0.86	7
3416	1.78	1	4611	0.81	1
3416	1.24	4	4623	0.70	4
3426	0.07	2	4623	0.80	9
3426	0.21	6	4623	0.60	6
3611	0.11	2	4711	0.50	9
3611	0.60	4	4711	0.60	2
3611	0.62	8	4911	0.92	4
3731	0.10	7	4911	1.10	1
3731	0.12	1	5111	0.92	1
3731	0.70	3	5221	0.42	9
3811	0.15	1	5426	0.50	7
3811	0.10	9	5426	0.50	6

(Table E-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5711	0.08	7	7526	0.71	1
5811	0.20	9	7622	0.80	8
5811	0.18	2	7622	0.70	3
6221	0.05	6	7622	1.00	2
6311	0.30	7	7722	0.30	7
6311	1.05	1	7722	0.45	6
6311	1.50	4	7722	0.33	8
6715	0.02	9	7813	0.82	2
6715	0.76	1	7813	0.60	4
6715	0.83	6	7813	1.84	1
6914	0.63	1	7824	1.70	8
7112	0.48	3	7824	1.67	9
7112	0.47	9	7914	0.63	1
7112	0.07	8	7914	0.41	9
7216	0.68	4	7922	0.10	9
7224	0.22	1	7922	0.48	8
7224	0.29	7	7922	0.60	3
7422	1.10	4	7926	0.65	3
7422	1.20	1	7926	0.83	9
7422	1.10	7	8111	0.20	7
7522	0.43	8	8111	0.35	1
7522	0.51	3	8222	0.77	8
7522	0.35	7	8222	1.10	4
7526	0.02	6	8222	0.98	1

(Table E-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
8222	0.87	3	9111	0.82	7
8326	0.64	9	9111	0.75	8
8326	0.82	7	9111	0.82	9
8326	0.96	4	9613	0.13	7
8512	0.80	6	9613	0.05	8
8512	0.70	3	9613	0.15	1
8512	0.55	8	9713	0.70	9
8622	0.90	7	9713	0.68	1
8622	1.00	6	9714	0.43	1
8622	1.22	8	9714	0.50	7
8822	0.80	8	9816	0.03	7
8822	0.74	3	9816	0.03	6

Table E-2. Sample 1, Combined Chlorine (1.00 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	1.64	2	1136	0.40	7
1	0.90	3	1136	0.50	6
1	0.96	4	1314	1.13	8
2	0.92	4	1314	0.32	6
2	1.64	2	1611	0.70	7
2	1.06	8	1611	1.05	9
3	1.07	3	2112	1.59	2
3	0.29	7	2112	1.27	1
3	1.04	8	2222	1.45	3
3	0.86	1	2222	1.48	8
5	0.10	8	2222	0.60	6
6	0.91	8	2223	0.53	7
7	1.75	2	2223	0.79	1
7	1.09	8	2311	0.92	4
8	1.04	2	2311	1.11	1
8	1.18	8	2311	1.10	3
9	0.40	6	2411	0.90	1
10	1.48	2	2411	0.97	4
10	1.51	3	2411	1.71	2
11	0.99	1	2411	1.03	8
1114	1.09	8	2926	0.82	9
1114	1.59	2	2926	0.95	1
1114	0.98	3	3122	1.12	8
1136	1.00	3	3122	0.20	7

(Table E-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3122	1.00	3	3811	1.10	2
3221	1.10	3	4212	0.40	7
3221	1.00	9	4212	1.12	3
3221	0.30	6	4212	0.30	6
3222	0.00	8	4421	0.45	9
3222	0.02	2	4421	1.27	1
3222	0.07	4	4511	0.65	9
3226	1.85	1	4511	1.10	3
3314	0.61	4	4516	0.58	6
3314	0.40	2	4516	1.71	2
3314	0.37	7	4516	0.90	4
3416	0.95	9	4611	0.25	7
3416	2.03	1	4611	1.19	1
3416	0.71	4	4623	0.70	9
3426	0.20	6	4623	1.00	4
3426	0.32	2	4623	0.60	6
3611	1.09	2	4711	0.50	9
3611	1.08	8	4711	0.20	2
3611	0.70	4	4911	0.84	1
3731	0.88	1	4911	1.02	4
3731	1.20	3	5111	1.01	1
3731	0.30	7	5221	1.05	9
3811	1.16	1	5426	0.50	7
3811	0.75	9	5426	0.50	6

(Table E-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5711	0.58	7	7622	0.89	2
5811	1.32	2	7622	1.06	8
5811	0.63	9	7622	1.05	3
6221	1.13	6	7722	0.20	7
6311	0.15	7	7722	0.20	6
6311	3.50	4	7722	1.07	8
6311	0.91	1	7813	1.38	2
6715	0.66	6	7813	0.42	4
6715	0.99	1	7813	0.11	1
6715	1.39	9	7824	0.03	9
6914	1.01	1	7824	0.04	8
7112	1.04	3	7914	0.77	1
7112	1.52	8	7914	1.00	9
7112	0.80	9	7922	2.52	8
7216	0.86	4	7922	5.40	3
7224	0.83	1	7922	6.60	9
7224	0.60	7	7926	1.17	3
7422	0.96	4	7926	0.99	9
7422	0.10	7	R111	1.56	1
7522	1.09	3	R111	0.50	7
7522	0.20	7	R222	1.02	1
7522	0.96	8	R222	1.10	4
7526	1.11	1	R222	1.15	7
7576	0.54	6	R222	1.06	8

(Table E-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
8326	0.21	7	9111	0.47	7
8326	0.32	9	9111	1.00	8
8512	0.40	6	9613	1.93	8
8512	1.00	3	9613	1.25	1
8512	1.30	8	9613	0.61	7
8622	0.35	7	9713	0.85	9
8622	0.20	6	9713	0.82	1
8622	0.00	8	9714	0.35	7
8822	0.95	8	9714	1.23	1
8822	1.00	3	9816	1.47	7
9111	0.93	9	9816	1.47	6

Table E-3. Sample 1, Total Chlorine (1.83 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	1.71	2	11	1.52	1
1	1.76	3	11	1.85	5
1	1.81	4	1114	1.47	8
2	1.70	4	1114	1.62	3
2	1.80	2	1114	1.75	2
2	1.82	8	1136	1.78	3
3	1.89	3	1136	1.30	7
3	1.08	7	1136	1.30	6
3	1.58	1	1314	1.14	6
3	1.84	8	1314	2.15	5
5	1.50	4	1314	1.98	8
5	1.60	8	1611	1.77	5
6	1.45	8	1611	1.40	7
6	1.83	5	1611	1.70	9
7	1.75	2	2112	2.32	1
7	1.79	8	2112	1.80	2
8	1.73	5	2112	1.52	5
8	1.82	8	2222	0.70	6
8	1.42	2	2222	1.60	8
9	1.20	6	2222	1.60	3
9	1.38	5	2223	1.08	5
10	1.53	3	2223	0.83	7
10	1.53	5	2223	1.07	1
10	1.50	2	2311	2.00	3

(Table E-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2311	2.04	1	3416	1.36	9
2311	1.84	4	3426	0.39	2
2411	1.68	1	3426	0.41	6
2411	1.75	4	3611	1.30	4
2411	1.79	8	3611	1.70	8
2411	1.77	2	3611	1.20	2
2926	1.99	1	3731	0.40	7
2926	1.97	9	3731	1.00	1
3122	0.80	7	3731	1.90	3
3122	1.49	8	3811	1.31	1
3122	1.70	3	3811	0.85	9
3221	1.40	9	3811	1.60	2
3221	1.50	3	4212	1.15	7
3221	0.60	6	4212	1.84	3
3222	1.35	8	4212	1.15	6
3222	1.32	2	4421	0.77	9
3222	1.22	4	4421	1.81	1
3226	1.92	1	4421	1.68	5
3226	1.50	6	4511	2.00	3
3314	0.54	7	4511	1.10	9
3314	0.77	4	4511	1.51	5
3314	0.55	2	4516	1.34	6
3416	1.05	4	4516	1.88	2
3416	3.81	1	4516	2.00	4

(Table E-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4611	1.11	7	6221	1.18	6
4611	1.50	5	6311	5.00	4
4611	2.00	1	6311	0.45	7
4623	1.50	9	6311	1.96	1
4623	1.70	4	6715	1.75	1
4623	1.20	6	6715	1.41	9
4711	0.30	2	6715	1.49	6
4711	0.95	5	6914	0.65	5
4711	1.00	9	6914	1.64	1
4911	1.94	4	7112	1.59	8
4911	1.94	1	7112	1.27	9
4911	1.50	5	7112	1.52	3
5111	1.93	1	7216	1.54	4
5111	1.72	5	7216	1.33	5
5221	1.47	9	7224	0.89	7
5221	1.18	5	7224	1.05	1
5426	1.60	5	7422	1.20	7
5426	1.00	7	7422	2.06	4
5426	1.00	6	7522	0.55	7
5711	0.66	7	7522	1.39	8
5711	1.33	5	7522	1.60	3
5811	1.50	2	7522	2.55	5
5811	0.88	5	7526	1.58	5
5811	0.83	9	7526	0.56	6

(Table E-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7526	1.82	1	8111	1.91	1
7622	1.86	8	8222	2.02	3
7622	1.89	2	8222	2.20	4
7622	1.75	3	8222	1.83	8
7722	0.50	7	8222	2.00	1
7722	0.65	6	8326	0.96	9
7722	1.40	8	8326	1.03	7
7813	1.88	5	8326	0.95	4
7813	1.02	4	8512	1.70	3
7813	1.95	1	8512	1.20	6
7813	2.20	2	8512	1.85	8
7824	1.70	9	8622	1.20	6
7824	1.74	8	8622	1.25	7
7914	1.40	1	8622	1.22	8
7914	1.36	5	8822	1.74	3
7914	1.41	9	8822	1.75	8
7922	3.00	8	8822	1.45	5
7922	6.00	3	9111	1.29	7
7922	6.70	9	9111	1.75	8
7926	1.82	9	9111	1.75	9
7926	1.81	5	9613	1.49	5
7926	1.82	3	9613	1.40	1
8111	1.35	5	9613	1.98	8
8111	0.70	7	9613	0.74	7

(Table E-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
9713	1.50	1	9714	1.66	1
9713	1.51	5	9816	1.50	6
9713	1.55	9	9816	1.58	5
9714	0.85	7	9816	1.50	7
9714	1.54	5			

Table E-4. Sample 2, Free Chlorine (0.80 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.80	2	1134	0.40	6
1	0.82	3	1136	0.63	3
1	0.72	4	1314	0.56	6
2	0.78	2	1314	0.55	8
2	0.80	4	1611	0.80	7
2	0.81	8	1611	0.75	9
3	0.60	1	2112	1.06	1
3	0.71	7	2112	1.03	2
3	0.70	8	2222	0.40	3
3	0.71	3	2222	0.02	6
5	0.60	8	2222	0.15	8
6	0.74	8	2223	0.44	1
7	0.70	2	2223	0.68	7
7	0.72	8	2311	0.34	4
8	0.33	2	2311	0.30	1
8	0.60	8	2311	0.33	3
9	0.40	6	2411	0.73	8
10	1.00	2	2411	0.75	1
10	0.98	3	2411	0.75	4
11	0.80	1	2411	0.72	2
1114	0.50	3	2926	0.65	9
1114	0.72	2	2926	0.75	1
1114	0.58	8	3122	0.38	8
1136	0.90	7	3122	0.90	7

(Table E-4 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3122	0.50	3	3811	0.49	1
3221	0.40	9	4212	0.78	6
3221	0.30	6	4212	0.73	7
3221	0.40	3	4212	0.78	3
3222	0.68	8	4421	0.55	1
3222	0.48	4	4421	0.53	9
3222	0.67	2	4511	0.45	9
3226	0.03	1	4511	0.60	3
3314	0.55	2	4516	1.08	4
3314	0.54	4	4516	1.08	6
3314	0.52	7	4516	0.96	2
3416	1.09	4	4611	0.70	7
3416	0.48	1	4611	0.75	1
3416	0.00	9	4623	0.60	9
3426	0.04	2	4623	0.55	4
3426	0.09	6	4623	0.50	6
3611	0.66	4	4711	0.45	2
3611	1.15	8	4711	0.80	9
3611	1.24	2	4911	0.86	1
3731	0.40	7	4911	0.82	4
3731	0.95	1	5111	0.66	1
3731	1.20	3	5221	0.00	9
3811	0.40	9	5426	0.30	6
3811	0.75	2	5426	0.30	7

(Table E-4 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5711	0.05	7	7526	0.03	6
5811	0.37	2	7622	0.59	8
5811	0.30	9	7622	0.59	3
6221	0.40	6	7622	0.62	2
6311	0.04	7	7722	0.59	8
6311	0.12	1	7722	0.45	6
6311	0.30	4	7722	0.25	7
6715	0.68	6	7813	0.94	2
6715	0.78	1	7813	0.96	1
6715	0.15	9	7813	0.44	4
6914	0.93	1	7824	0.78	8
7112	0.36	9	7824	0.72	9
7112	0.37	3	7914	0.57	1
7112	0.33	8	7914	0.32	9
7216	0.60	4	7922	7.15	8
7224	0.20	7	7922	6.48	3
7224	0.20	1	7922	1.50	9
7422	1.20	4	7926	0.62	9
7422	1.30	1	7926	0.68	3
7422	1.20	7	8111	0.30	7
7522	0.61	8	8111	0.63	1
7522	0.60	3	8222	0.90	8
7522	0.45	7	8222	1.02	3
7526	0.56	1	8222	1.10	4

(Table E-4 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
8222	0.96	1	9111	0.75	8
8326	0.45	9	9111	0.85	9
8326	0.50	4	9111	0.86	7
8326	0.48	7	9613	0.08	7
8512	0.85	3	9613	0.05	8
8512	0.80	8	9613	0.10	1
8512	0.85	6	9713	0.60	1
8622	1.20	6	9713	0.55	9
8622	1.36	8	9714	0.57	7
8622	1.10	7	9714	0.46	1
8822	0.22	8	9816	0.15	6
8822	0.23	3	9816	0.15	7

Table E-5. Sample 2, Combined Chlorine (0.04 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.01	2	1136	0.20	7
1	0.01	3	1136	0.30	6
1	0.03	4	1314	0.24	8
2	0.22	2	1314	0.08	6
2	0.18	4	1611	0.05	9
2	0.30	8	2112	0.03	1
3	0.11	3	2222	0.36	6
3	0.00	7	2222	0.39	8
3	0.12	8	2222	0.10	3
3	0.02	1	2223	0.00	1
5	0.20	8	2223	0.00	7
6	0.08	8	2311	0.30	4
7	0.05	2	2311	0.47	1
7	0.05	8	2311	0.44	3
8	0.10	8	2411	0.03	4
8	0.17	2	2411	0.03	8
9	0.00	6	2411	0.00	1
10	0.01	3	2411	0.15	2
10	0.04	2	2926	0.00	9
11	0.07	1	2926	0.03	1
1114	0.08	2	3122	0.10	7
1114	0.09	8	3122	0.10	3
1114	0.03	3	3122	0.12	8
1136	0.05	3	3221	0.00	9

(Table E-5 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3221	0.00	3	4212	0.10	7
3221	0.00	6	4212	0.00	6
3222	0.10	4	4421	0.09	1
3222	0.04	8	4421	0.04	9
3222	0.01	2	4511	0.15	3
3226	0.85	1	4511	0.40	9
3314	0.08	7	4516	0.00	6
3314	0.03	2	4516	0.00	2
3314	0.09	4	4611	0.15	7
3416	0.79	4	4611	0.10	1
3416	0.77	1	4623	0.00	4
3416	0.18	9	4623	0.00	6
3426	0.12	2	4623	0.00	9
3426	0.05	6	4711	0.25	2
3611	0.00	4	4711	0.00	9
3611	0.00	8	4911	0.02	1
3611	0.30	2	4911	0.04	4
3731	0.05	7	5111	0.00	1
3731	0.13	1	5221	0.64	9
3731	0.10	3	5426	0.20	7
3811	0.05	2	5426	0.20	6
3811	0.08	1	5711	0.51	7
3811	0.00	9	5811	0.03	2
4212	0.02	3	5811	0.00	9

(Table E-5 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6221	6.40	6	7722	0.35	6
6311	0.42	1	7722	0.25	7
6311	0.00	4	7813	0.24	2
6311	0.08	7	7824	0.08	8
6715	0.02	6	7824	0.06	9
6715	0.55	9	7914	0.04	1
6715	0.03	1	7914	0.50	9
6914	0.07	1	7926	0.00	9
7112	0.21	8	7926	0.00	3
7112	0.07	3	8111	0.07	1
7112	0.00	9	8111	0.20	7
7224	0.60	7	8222	0.00	3
7224	0.78	1	8222	0.00	8
7422	0.00	7	8222	0.00	1
7422	0.10	1	8222	0.00	4
7522	0.10	8	8326	0.07	9
7522	0.09	3	8326	0.05	4
7522	0.20	7	8326	0.09	7
7526	0.45	6	8512	0.00	6
7526	0.12	1	8512	0.15	8
7622	0.03	3	8512	0.00	3
7622	0.23	2	8622	0.00	8
7622	0.02	8	8622	0.20	6
7722	0.00	8	8622	0.20	7

(Table E-5 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
8822	0.58	8	9613	0.70	8
8822	0.28	3	9713	0.00	9
9111	0.10	8	9713	0.00	1
9111	0.10	7	9714	0.12	7
9111	0.04	9	9714	0.32	1
9613	0.33	7	9816	0.63	7
9613	0.52	1	9816	0.61	6

Table E-6. Sample 2, Total Chlorine (0.84 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.81	2	11	0.81	5
1	0.83	3	11	0.87	1
1	0.75	4	1114	0.53	3
2	1.00	2	1114	0.80	2
2	0.98	4	1114	0.47	8
2	1.11	8	1136	0.70	7
3	0.62	1	1136	0.68	3
3	0.71	7	1136	0.70	6
3	0.82	8	1314	0.64	6
3	0.82	3	1314	0.79	8
5	0.68	4	1314	0.85	5
5	0.80	8	1611	0.85	5
6	0.82	8	1611	0.75	7
6	0.75	5	1611	0.80	9
7	0.75	2	2112	1.09	1
7	0.77	8	2112	0.92	5
8	0.70	8	2112	1.02	2
8	0.50	2	2222	0.54	8
8	0.69	5	2222	0.38	6
9	0.40	6	2222	0.50	3
9	0.37	5	2223	0.72	5
10	1.00	5	2223	0.68	7
10	1.04	2	2223	0.44	1
10	0.99	3	2311	0.77	3

(Table E-6 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2311	0.77	1	3416	0.18	9
2311	0.64	4	3426	0.16	2
2411	0.76	8	3426	0.14	6
2411	0.87	2	3611	0.94	2
2411	0.75	1	3611	1.15	8
2411	0.78	4	3611	0.66	4
2926	0.65	9	3731	0.45	7
2926	0.78	1	3731	1.30	3
3122	0.50	8	3731	1.08	1
3122	0.60	7	3811	0.57	1
3122	0.60	3	3811	0.80	2
3221	0.40	9	3811	0.40	9
3221	0.40	3	4212	0.78	6
3221	0.30	6	4212	0.80	3
3222	0.58	4	4212	0.83	7
3222	0.72	8	4421	0.57	9
3222	0.68	2	4421	0.64	1
3226	0.88	1	4421	0.59	5
3226	0.50	6	4511	0.75	3
3314	0.58	2	4511	0.53	5
3314	0.60	7	4511	0.85	9
3314	0.63	4	4516	1.04	4
3416	1.88	4	4516	1.08	6
3416	1.25	1	4516	0.96	2

(Table E-6 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4611	0.85	7	6221	6.80	6
4611	0.44	5	6311	0.12	7
4611	0.85	1	6311	0.30	4
4623	0.55	4	6311	0.54	1
4623	0.50	6	6715	0.81	1
4623	0.60	9	6715	0.70	6
4711	0.80	9	6715	0.70	9
4711	0.70	2	6914	0.70	5
4711	0.45	5	6914	1.00	1
4911	0.74	5	7112	0.44	3
4911	0.88	1	7112	0.36	9
4911	0.86	4	7112	0.54	8
5111	0.66	1	7216	0.52	5
5111	0.76	5	7216	0.59	4
5221	0.25	5	7224	0.80	7
5221	0.64	9	7224	0.98	1
5426	0.53	5	7422	1.40	1
5426	0.50	7	7422	1.13	4
5426	0.50	6	7422	1.20	7
5711	0.56	7	7522	0.69	3
5711	0.56	5	7522	0.71	8
5811	0.35	5	7522	0.69	5
5811	0.40	2	7522	0.65	7
5811	0.30	9	7526	0.68	1

(Table E-6 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7526	0.48	6	9111	0.50	7
7526	0.72	5	9111	0.70	1
7622	0.85	2	9222	0.90	8
7622	0.62	3	9222	1.02	3
7622	0.61	8	9222	0.96	1
7722	0.50	7	9222	1.10	4
7722	0.59	8	9326	0.52	9
7722	0.80	6	9326	0.57	7
7813	0.42	4	9326	0.55	4
7813	0.76	1	9512	0.95	8
7813	0.69	5	9512	0.85	3
7813	1.18	2	9512	0.85	6
7824	0.78	9	9622	1.30	7
7824	0.86	8	9622	1.40	6
7914	0.81	5	9622	1.36	8
7914	0.82	9	9822	0.41	5
7914	0.61	1	9822	0.51	3
7922	0.08	3	9822	0.80	8
7922	0.05	8	9111	0.96	7
7922	0.00	9	9111	0.85	8
7926	0.62	9	9111	0.89	9
7926	0.69	5	9613	0.62	1
7926	0.68	3	9613	0.67	5
8111	0.60	5	9613	0.75	8

(Table E-6 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
9613	0.41	7	9714	0.78	1
9713	0.49	5	9714	0.69	7
9713	0.60	1	9816	0.70	5
9713	0.55	9	9816	0.76	6
9714	0.70	5	9816	0.78	7

Table E-7. Sample 3, Free Chlorine (0.04 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.00	2	1611	0.10	7
1	0.01	3	1611	0.10	9
1	0.00	4	2112	0.19	1
2	0.10	2	2112	0.14	2
2	0.12	4	2222	0.00	8
2	0.36	8	2222	0.00	3
3	0.00	1	2222	0.00	6
3	0.00	7	2223	0.15	1
3	0.00	8	2223	0.20	7
3	0.00	3	2311	0.42	1
5	0.00	8	2311	0.50	3
6	0.05	8	2311	0.48	4
7	0.00	8	2411	0.00	4
7	0.00	2	2411	0.01	2
8	0.00	8	2411	0.01	1
8	0.00	2	2411	0.02	8
10	0.00	2	2926	0.00	9
10	0.00	3	2926	0.00	1
11	0.10	1	3122	0.10	7
1114	0.05	8	3122	0.00	8
1114	0.03	3	3122	0.00	3
1114	0.04	2	3221	0.00	6
1314	0.00	8	3221	0.00	9
1314	0.01	6	3221	0.00	3

(Table E-7 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3222	0.00	8	4421	0.00	9
3222	0.00	2	4421	0.00	1
3222	0.00	4	4511	0.00	3
3226	0.05	1	4511	0.00	9
3314	0.05	2	4516	0.00	4
3314	0.07	4	4516	0.00	2
3314	0.06	7	4516	0.28	6
3416	0.68	4	4611	0.50	1
3416	0.02	9	4611	0.45	7
3416	0.53	1	4623	0.00	4
3426	0.25	6	4623	0.00	6
3426	0.04	2	4623	0.00	9
3611	0.00	2	4711	0.00	2
3611	0.00	4	4711	0.00	9
3611	0.00	8	4911	0.12	1
3731	0.10	7	4911	0.00	4
3731	0.00	3	5111	0.17	1
3731	0.00	1	5221	0.00	9
3811	0.00	9	5711	0.05	7
3811	0.67	1	5811	0.10	2
3811	0.30	2	5811	0.00	9
4212	0.05	6	6221	0.07	6
4212	0.12	7	6311	0.40	4
4212	0.00	3	6311	0.05	7

(Table E-7 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6311	0.02	1	7722	0.10	7
6715	0.02	6	7813	0.58	2
6715	0.02	1	7813	0.04	4
6715	0.00	9	7813	0.12	1
6914	0.10	1	7824	0.58	8
7112	0.05	8	7824	0.54	9
7112	0.03	3	7914	0.00	9
7112	0.43	9	7914	0.05	1
7216	0.00	4	7922	0.20	9
7224	0.10	7	7922	0.65	8
7224	0.10	1	7922	0.23	3
7422	0.50	1	7926	0.02	3
7422	0.10	4	7926	0.00	9
7422	0.50	7	8111	0.10	1
7522	0.03	3	8111	0.00	7
7522	0.42	8	8222	0.00	4
7522	0.05	7	8222	0.00	8
7526	0.14	6	8222	0.00	1
7526	0.70	1	8222	0.00	3
7622	0.00	8	8326	0.07	7
7622	0.00	2	8326	0.05	9
7622	0.00	3	8326	0.00	4
7722	0.40	8	8512	0.00	3
7722	0.15	6	8512	0.00	8

(Table E-7 continued)

LAB. NO.	RESULTS	METHOD
8512	0.00	6
8622	0.14	8
8622	0.05	6
8622	0.05	7
8822	0.00	3
8822	0.05	8
9111	0.00	8
9111	0.00	7
9111	0.00	9
9613	0.30	7
9613	0.08	8
9613	0.15	1
9713	0.00	9
9713	0.00	1
9714	0.40	7
9714	0.06	1
9816	0.02	6
9816	0.02	7

Table E-8. Sample 3, Combined Chlorine (0.60 mg/l)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.65	2	1611	0.60	7
1	0.67	3	1611	0.55	9
1	0.67	4	2112	0.95	1
2	0.64	4	2112	0.81	2
2	0.62	2	2222	0.72	3
2	0.52	8	2222	0.60	6
3	0.69	3	2222	0.70	8
3	0.61	7	2223	0.00	1
3	0.48	1	2223	0.02	7
3	0.70	8	2311	0.14	4
5	0.30	8	2311	0.00	3
6	0.59	8	2311	0.30	1
7	0.68	2	2411	0.48	1
7	0.70	8	2411	0.56	2
8	0.22	2	2411	0.47	4
8	0.63	8	2411	0.46	8
10	0.53	3	2926	0.33	9
10	0.60	2	2926	0.47	1
11	0.67	1	3122	0.40	7
1114	0.47	2	3122	0.44	8
1114	0.35	3	3122	0.55	3
1114	0.29	8	3221	0.30	6
1314	0.49	8	3221	0.40	9
1314	0.39	6	3221	0.40	3

(Table E-8 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3222	0.60	2	4421	0.93	1
3222	0.70	8	4421	0.62	9
3222	0.55	4	4511	0.55	3
3226	0.60	1	4511	0.50	9
3314	0.20	2	4516	0.60	6
3314	0.22	4	4516	0.84	2
3314	0.24	7	4516	0.83	4
3416	1.45	4	4611	0.22	1
3416	0.40	9	4611	0.29	7
3416	1.37	1	4623	0.10	6
3426	0.52	2	4623	0.20	4
3426	0.28	6	4623	0.40	9
3611	0.62	2	4711	0.00	2
3611	0.50	4	4711	0.00	9
3611	0.60	8	4911	0.70	4
3731	0.80	1	4911	0.59	1
3731	0.70	3	5111	0.26	1
3731	0.20	7	5221	0.47	9
3811	0.25	1	5711	0.37	7
3811	0.70	2	5811	0.62	2
3811	0.37	9	5811	0.35	9
4212	0.53	7	6221	0.68	6
4212	0.70	3	6311	0.81	1
4212	0.60	6	6311	1.10	4

(Table E-8 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6311	0.74	7	7722	0.40	6
6715	0.35	9	7813	0.42	2
6715	0.57	1	7813	0.80	1
6715	0.55	6	7813	0.44	4
6914	0.63	1	7824	0.06	9
7112	0.03	9	7824	0.02	8
7112	0.54	3	7914	0.44	1
7112	0.42	8	7914	0.37	9
7216	1.05	4	7922	3.20	8
7224	0.35	7	7922	4.37	3
7224	0.65	1	7922	1.30	9
7422	0.60	7	7926	0.42	9
7422	0.93	4	7926	0.50	3
7422	0.80	1	8111	0.42	1
7522	0.60	7	8111	0.40	7
7522	0.70	3	8222	0.77	3
7522	0.17	8	8222	0.75	8
7526	0.22	6	8222	0.90	1
7526	0.27	1	8222	0.76	4
7622	0.50	3	8326	0.45	9
7622	0.49	2	8326	0.55	7
7622	0.42	8	8326	0.73	4
7722	0.00	8	8512	0.60	8
7722	0.20	7	8512	0.45	6

(Table E-8 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
8512	0.50	3	9613	0.30	1
8622	0.60	6	9613	0.10	7
8622	0.53	8	9613	0.42	8
8622	0.60	7	9713	0.60	9
8822	0.61	3	9713	0.60	1
8822	0.65	8	9714	0.67	1
9111	0.77	7	9714	0.18	7
9111	0.76	9	9816	0.53	6
9111	0.75	8	9816	0.58	7

Table E-9. Sample 3, Total Chlorine (0.64 mg/1)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.65	2	11	0.77	1
1	0.68	3	1114	0.34	8
1	0.67	4	1114	0.38	3
2	0.72	2	1114	0.51	2
2	0.76	4	1136	0.60	7
2	0.88	8	1136	0.57	3
3	0.69	3	1136	0.60	6
3	0.61	7	1314	0.49	8
3	0.70	8	1314	0.40	6
3	0.48	1	1314	0.40	5
5	0.40	4	1611	0.65	5
5	0.30	8	1611	0.70	7
6	0.48	5	1611	0.65	9
6	0.64	8	2112	1.14	1
7	0.70	8	2112	0.95	2
7	0.68	2	2112	0.78	5
8	0.61	5	2222	0.72	3
8	0.63	8	2222	0.60	6
8	0.22	2	2222	0.70	8
9	0.05	5	2223	0.33	5
10	0.51	5	2223	0.22	7
10	0.53	3	2223	0.15	1
10	0.60	2	2311	0.50	3
11	0.88	5	2311	0.62	4

(Table E-9 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2311	0.72	1	3426	0.56	2
2411	0.57	2	3426	0.53	6
2411	0.49	1	3611	0.60	8
2411	0.47	4	3611	0.50	4
2411	0.48	8	3611	0.62	2
2926	0.33	9	3731	0.70	3
2926	0.47	1	3731	0.30	7
3122	0.55	3	3731	0.80	1
3122	0.44	8	3811	1.00	2
3122	0.50	7	3811	0.92	1
3221	0.30	6	3811	0.37	9
3221	0.40	9	4212	0.65	6
3221	0.40	3	4212	0.65	7
3222	0.55	4	4212	0.70	3
3222	0.70	8	4421	0.71	5
3222	0.60	2	4421	0.62	9
3226	0.65	1	4421	0.93	1
3226	0.24	6	4511	0.50	9
3314	0.25	2	4511	0.55	3
3314	0.30	7	4511	0.35	5
3314	0.29	4	4516	0.84	2
3416	2.13	4	4516	0.88	6
3416	0.42	9	4516	0.83	4
3416	1.90	1	4611	0.74	7

(Table E-9 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4611	0.58	5	6311	0.83	1
4611	0.72	1	6311	1.50	4
4623	0.20	4	6311	0.79	7
4623	0.40	9	6715	0.59	1
4623	0.10	6	6715	0.57	6
4711	0.00	9	6715	0.35	9
4711	0.00	5	6914	0.49	5
4711	0.00	2	6914	0.73	1
4911	0.71	1	7112	0.47	8
4911	0.69	5	7112	0.46	9
4911	0.70	4	7112	0.57	3
5111	0.43	1	7216	0.66	5
5111	0.50	5	7216	1.05	4
5221	0.47	9	7224	0.45	7
5221	0.24	5	7224	0.75	1
5426	0.60	5	7422	1.03	4
5426	0.50	7	7422	1.30	1
5426	0.50	6	7422	1.10	7
5711	0.49	5	7522	0.73	3
5711	0.42	7	7522	0.70	5
5811	0.35	9	7522	0.59	8
5811	0.72	2	7522	0.65	7
5811	0.44	5	7526	0.97	1
6221	0.75	6	7526	0.36	6

(Table E-9 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7526	0.52	5	8111	0.40	7
7622	0.42	8	8222	0.75	8
7622	0.50	3	8222	0.76	4
7622	0.49	2	8222	0.90	1
7722	0.30	7	8222	0.77	3
7722	0.55	6	8326	0.73	4
7722	0.40	8	8326	0.50	9
7813	1.00	2	8326	0.62	7
7813	0.92	1	8512	0.50	3
7813	0.67	5	8512	0.45	6
7813	0.48	4	8512	0.60	8
7824	0.60	8	8622	0.65	7
7824	0.60	9	8622	0.67	8
7914	0.33	5	8622	0.65	6
7914	0.49	1	8822	0.61	3
7914	0.37	9	8822	0.38	5
7922	3.85	8	8822	0.70	8
7922	4.60	3	9111	0.75	8
7922	1.50	9	9111	0.76	9
7926	0.52	3	9111	0.77	7
7926	0.42	9	9613	0.50	8
7926	0.50	5	9613	0.40	7
8111	0.52	1	9613	0.48	5
8111	0.36	5	9613	0.45	1

(Table E-9 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
9713	0.57	5	9714	0.73	1
9713	0.60	9	9816	0.60	7
9713	0.60	1	9816	0.44	5
9714	0.58	7	9816	0.55	6
9714	0.61	5			

APPENDIX F.

GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms defined as they are used in this report is presented to ensure uniformity of understanding.

Arithmetic mean — The sum of the sample results divided by the number of results in the sample. Let X_i ($i = 1, 2, \ldots, n$) denote the i^{th} results in a sample of n results. The arithmetic mean denoted $\overline{X}$ is given by $\overline{X} = \sum_{i=1}^{n} \frac{X_i}{n}$.

Median — Halfway point in the results when they have been arranged in order of magnitude (the middle result of an odd number of results, or the average of the middle two for an even number).

Accuracy — The correctness of a measurement, or the degree of correspondence between the results and the true value (actual amount added).

Measures of accuracy — Measures that relate to the difference between the mean of the results and the true value when the latter is known or assumed. The following measures apply:

Mean error — The average difference with regard to sign between the results and the true value. Equivalently, the difference between the mean of the results and the true value (T. V.).

$$\text{Mean error} = \overline{X} - \text{T. V.}$$

Relative error — The absolute value of the mean error expressed as a percentage of the true value.

$$\text{Relative error} = \frac{|\overline{X} - \text{T. V.}|}{\text{T. V.}} \times 100$$

Precision — The reproducibility of sample results or the degree of agreement among the results.

Measures of precision

Measures of the variation among the sample results themselves, i.e., the spread or dispersion of the results without regard to the true value. The following measures apply.

Sample variance — Sum of squared deviations of the sample results from their mean divided by one less than the number of results in the sample. The sample variance denoted s^2 is given by

$$s^2 = \frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n - 1}$$

where n is the number of results.

Sample standard deviation — Square root of the sample variance.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n - 1}}$$

Relative standard deviation (coefficient of variation) — Sample standard deviation expressed as a percentage of the mean.

$$\text{Rel. Std. Dev.} = \frac{s}{\overline{X}} \times 100$$

Range — The difference between the largest and smallest results in the sample.

Confidence limits — Limits within which the true mean, μ, of the population (the theoretically infinite number of possible replications of the analysis) will lie with probability equal to $1 - \alpha$, where α is the probability that the limits do not contain the true mean. The upper and lower $1 - \alpha$ confidence limits are given by

$$\text{Confidence limits} = \overline{X} \pm t_{\alpha/2} s/\sqrt{n}$$

where $\overline{X}$ and s are the sample mean and standard deviation, $t_{\alpha/2}$ is the upper $\alpha/2$ point of "Student's" t-distribution, and n is the number of results in the sample used to compute $\overline{X}$.

Tolerance limits — Limits within which one can state with probability γ that at least a proportion P of the entire population will lie. The upper and lower tolerance limits are given by

$$\text{Tolerance limits} = \overline{X} \pm Ks,$$

where K is the factor for two-sided tolerance limits for normal populations.[1] The value of K depends upon the chosen values of γ and P.

REFERENCES

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APPENDIX G.

TESTS FOR NORMALITY AND REJECTION OF OUTLIERS

Test for normality

The Kolmogorov-Smirnov goodness-of-fit test was used to determine whether the observations reported could reasonably be thought to have come from a normal distribution.[1]

Briefly, the test involves computing the observed cumulative frequency distribution (the percent of values less than or equal to each value in the distribution) and comparing it with the theoretical normal cumulative frequency distribution. The point at which the two distributions, theoretical and observed, show greatest divergence is determined. Reference of the value of the divergence to a table of critical values for the Kolmogorov-Smirnov goodness-of-fit test indicates whether such a large divergence is likely on the basis of chance. If such a large divergence is not likely, the distribution is designated as nonnormal; otherwise the distribution is designated as normal.

Tests for rejection of outliers

1. If the distribution is designated as nonnormal, the suspected outlier (the farthest value from the mean) is rejected only if the distance between it and the mean is greater than three standard deviations; otherwise the suspected outlier is accepted.

2. If the distribution is designated as normal and the sample size is less than or equal to 30, the suspected outlier, the farthest value from the mean, is tested for rejection by a method developed by Dixon.[2] Briefly, this test involves computing a ratio that compares the distance of the suspected value being tested from its neighbors with the range of all, or most all, of the observations (depending on the total number of suspected values in the sample). Reference of the ratio to a table of critical values for test ratios for gross errors indicates whether such a large ratio is likely on the basis of chance. If the ratio is greater than or equal to the critical value, the probability that the suspected outlier is from the sample distribution is small; hence, the outlier is rejected. If the ratio is less than the critical value, the suspected outlier probably came from the sample distribution; hence, the suspected outlier is accepted.

3. If the distribution is designated as normal, and the sample size is greater than 30, the suspected outlier is tested for rejection by a method developed by Santner.[3] This method employs the statistic, $\frac{\overline{X} - X_o}{s}$, where $\overline{X}$ is the sample mean, X_o is the suspected outlier (the

farthest value from the mean) and s is the sample standard deviation. This statistic is compared with a table of critical values to determine whether its value is larger than would be expected on the basis of chance. If the statistic is greater than or equal to the critical value, the suspected outlier is rejected; otherwise, the suspected outlier is accepted.

Application of tests for normality and for rejection of outliers to ARS studies

The test for normality and the subsequent test for rejection of outliers are applied to the observed data in two ways: first, to each method for a given substance at a given concentration; then to a given substance at a given concentration regardless of method. In either case, it is first necessary to determine whether the original distribution is normal or nonnormal. If the original distribution is designated as nonnormal, method 1 is used to test for rejection of the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests for normality or rejection of outliers are made, and the distribution is designated as nonnormal. On the other hand, if the suspected outlier is rejected, the new distribution, which excludes the rejected observation, is then tested for normality. If the new distribution is nonnormal, the next suspected outlier is tested for rejection by method 1. This cycle of testing for normality and testing for rejection of outliers continues until a suspected value is not rejected or the test for normality designates the distribution as normal. If the distribution is designated as normal, subsequent tests for rejection of outliers made by method 2 or 3 are the same as if the original distribution had been normal. This case is discussed next.

If the original distribution is designated as normal or a new distribution that was originally nonnormal is designated as normal after the rejection of one or more outliers, and if the number of observations is not greater than 30, then method 2 is used to test for rejection the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution is tested for rejection, and so on until the suspected value of a new distribution is not rejected; when this occurs, no further tests are made, and the final distribution is designated as normal. On the other hand, if the number of observations in the original distribution is greater than 30, method 3 is used to test the suspected outlier for rejection. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, than the suspected outlier farthest from the mean of the new distribution, which excludes the rejected value, is tested for rejection. Testing for outliers continues by this method until a suspected outlier is not rejected or the number of

observations is no longer greater than 30, in which case, method 2 is used for testing for rejection of any remaining suspected outliers.

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APPENDIX H.

STATISTICAL COMPARISON OF METHODS WITH RESPECT TO PRECISION AND ACCURACY

The methods are compared in two ways with respect to precision and accuracy. In the first case, two methods are compared at a given concentration with respect to precision and to accuracy. The unknown variances, σ_1^2 and σ_2^2 (estimated by the sample variances, s_1^2 and s_2^2), of the two methods are first compared by the F-test[1] to determine whether there is a significant difference in the precision of the two methods. The unknown means, μ_1 and μ_2 (estimated by the sample means, $\overline{X}_1$ and $\overline{X}_2$), of the two methods are then compared by the t-test[2] to determine whether there is a significant difference in the accuracy of the two methods. The t-test employed is based on the result of the F-test. These two tests of hypotheses will produce one of the following results.

Outcome 1: $\sigma_1^2 = \sigma_2^2, \mu_1 = \mu_2$

Outcome 2: $\sigma_1^2 = \sigma_2^2, \mu_1 \neq \mu_2$

Outcome 3: $\sigma_1^2 \neq \sigma_2^2, \mu_1 = \mu_2$

Outcome 4: $\sigma_1^2 \neq \sigma_2^2, \mu_1 \neq \mu_2$

In outcome 1, we conclude that the sample results do not indicate that a significant difference in either precision or accuracy exists between the two methods.

In outcome 2, we conclude that there is no indication of a significant difference in precision between the two methods, but there is a significant difference in the accuracy of the two methods; specifically, the method whose sample mean is closer to the true value is deemed the more accurate. In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the two methods, but the method with the smaller sample variance is the more precise.

In outcome 4, we conclude that there is a significant difference in the precision and in the accuracy of the two methods. The method with the smaller sample variance is the more precise, and the method whose sample mean is closer to the true value is the more accurate.

In the second case, more than two methods are compared at a given level of concentration with respect to precision and accuracy. Bartlett's

Test[3] is used first to test the hypothesis of equality of the unknown variances, σ_i^2, of the methods in order to compare the precision of the methods. If we conclude that the precision is the same, the Analysis of Variance[4] is then used to test whether a significant difference exists among the means, μ_i, in order to compare the accuracy of the methods. If there is a significant difference among the means, Duncan's Multiple Range Test[5, 6] is used to determine which method means differ significantly. If the precision is not the same, then the Kruskal-Wallis One-way Analysis of Variance by Ranks[7] is used to determine whether a significant difference exists among the means in order to compare the accuracy of the methods.

Once again, there are basically four possible outcomes for the above tests of hypotheses.

Outcome 1: all σ_i^2 are equal, all μ_i are equal

Outcome 2: all σ_i^2 are equal, not all μ_i are equal

Outcome 3: not all σ_i^2 are equal, all μ_i are equal

Outcome 4: not all σ_i^2 are equal, not all μ_i are equal

In outcome 1, we conclude that the sample results do not indicate a significant difference in either the precision or the accuracy of the methods.

In outcome 2, we conclude that there is no indication of a significant difference in the precision of the methods; however, at least one method does differ significantly from the rest with respect to accuracy, and Duncan's Multiple Range Test indicates which methods differ. For example, in comparing four methods, we might conclude $\mu_1 = \mu_2$ and $\mu_3 = \mu_4$, but μ_1 and μ_2 differ significantly from μ_3 and μ_4; or we might conclude that $\mu_1 = \mu_2 = \mu_3$, but μ_4 differs significantly from μ_1, μ_2, and μ_3.

In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the methods, but at least one method differs significantly from the rest with respect to precision.

In outcome 4, we conclude that the methods differ significantly with respect to both precision and accuracy.

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APPENDIX I.

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Alabama State Department of Public Health, Montgomery
Alabama Water Improvement Commission, Montgomery
Arizona State Department of Health, Phoenix
Arkansas Pollution Control Commission, Little Rock
Arkansas State Department of Health, Little Rock
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California State Department of Public Health, Los Angeles
California State Department of Public Health, Air and Industrial Hygiene Laboratory, Berkeley
California State Department of Public Health, Sanitation and Radiation Laboratory, Berkeley
Colorado Department of Public Health, Denver
Connecticut State Department of Health, Hartford
Delaware Water and Air Resources Commission, Dover
District of Columbia Department of Public Health, Washington, D.C.
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Florida State Board of Health, Jacksonville
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